UNIVERSITY OF HAWAII
LIBRARY
APR 4 '56

GEOCHIMICA ET COSMOCHIMICA ACTA

EDITORIAL ADVISORY BOARD

L. H. AHRENS-CAMBRIDGE, MASS · T. BARTH-OSLO · N. L. BOWEN-WASHINGTON, D. C. · A. F. BUDDINGTON-PRINCETON, N. J. · L. CAPDECOMME-TOULOUSE · E. J. CONWAY-DUBLIN · P. ESKOLA-HELSINKI · P. GALLITELLI-MODENA · J. GOGUEL-PARIS · D. GUIMARÃES-BELO HORIZONTE · A. HADDING-LUND · O. HAHN-GÖTTINGEN · H. W. HARVEY-PLYMOUTH · F. HEIDE-JENA · A. HOLMES-EDINBURGH · G. E. HUTCHINSON-NEW HAVEN, CONN. · W. Q. KENNEDY-LEEDS · PH. H. KUENEN-GRONINGEN · S. LANDERGREN-STOCKHOLM · F. MACHATSCHKI-VIENNA · B. H. MASON-BLOOMINGTON, IND. · A. MUIR-HARPENDEN · P. NIGGLI-ZÜRICH · J. ORCEL-PARIS · K. RANKAMA-HELSINKI · E. REINHARD-BASLE · TH. G. SAHAMA-HELSINKI · C. E. TILLEY-CAMBRIDGE · H. C. UREY-CHICAGO · T. VOGT-TRONDHEIM · W. WAHL-HELSINKI · T. WATANABE-TOKYO · F. WHIPPLE-CAMBRIDGE, MASS. · R. WILDT-NEW HAVEN, CONN.

EDITORS

C. W. CORRENS, GÖTTINGEN
E. INGERSON, WASHINGTON
S. R. NOCKOLDS, CAMBRIDGE
F. A. PANETH, DURHAM
L. R. WAGER, OXFORD
F. E. WICKMAN, STOCKHOLM

VOL 3 NO. 1

1953

PERGAMON PRESS LTD · LONDON

Geochim. et Cosmochim. Acta
E 351

GEOCHIMICA ET COSMOCHIMICA ACTA

EDITORS

PROF. C. W. CORRENS, *Sedimentpetrographisches Institut der Universität, Lotzestr. 13, Göttingen, British Zone, Germany.*

DR. E. INGERSON, *United States Department of the Interior, U. S. Geological Survey, Washington 25, D. C., U.S.A.*

DR. S. R. NOCKOLDS, *Department of Mineralogy and Petrology, The University, Cambridge, England.*

PROF. F. A. PANETH, F. R. S., *Londonderry Laboratory for Radiochemistry, The University, South Road, Durham, England.*

PROF. L. R. WAGER, F.R.S., *Department of Geology and Mineralogy, The University, Oxford, England.*

PROF. F. E. WICKMAN, *Naturhistoriska Riksmuseets, Mineralogiska Avdelning, Stockholm 50, Sweden.*

1953 VOLUME 3 NUMBER 1

CONTENTS

Page

L. H. AHRENS: The use of ionization potentials. Part 2. Anion affinity and geochemistry 1

R. A. COOLEY, A. V. MARTIN, C. FELDMAN and J. GILLESPIE: The hafnium to zirconium abundance ratio and specific radioactivity of some ores 30

H. W. FAIRBAIRN, L. H. AHRENS and LORRAINE G. GORFINKLE: Minor element content of Ontario diabase 34

P. SCHAUFELBERGER: Was ist Laterit? 47

Publishing Offices: 2, 3 & 5 Studio Place, Kinnerton Street, London S.W. 1 (SLOane 8157–9). Subscription per volume (including postage) £ 4 4s. (U.S.A. $ 11·80). *Distributors:* All countries except Germany — *Lange, Maxwell & Springer Ltd., 41–45 Neal Street, London W.C. 2.* Germany — *Lange & Springer, Reichpietschufer 20, Berlin W 35.*

PERGAMON PRESS LTD., 2, 3 & 5 STUDIO PLACE, KINNERTON STREET, LONDON S.W. 1

Geochimica et Cosmochimica Acta, 1953, Vol. 3, pp. 1 to 29. Pergamon Press Ltd. London

The use of ionization potentials

Part 2. Anion affinity and geochemistry

L. H. AHRENS

Department of Geology and Geophysics, Massachusetts Institute of Technology

(Recieved 3 May 1952)

ABSTRACT

The nature of bonds and their mechanism of formation are briefly discussed. It is concluded that the so-called ionic approach be used for interpreting properties of metal-nonmetal compounds irrespective of whether the bonds are dominantly covalent or dominantly ionic. It is assumed that the history of each metal-nonmetal reaction passes through a transitory stage in which the properties of free ions play a dominant role in determining the properties of the equilibrium product. *Anion affinity* is defined as the power of a cation for attracting anions in the transitory state, and the ionization potential (first for monovalent cations, second for divalent cations, and so on) is used as a relative measure of anion affinity. Various topics of geochemical interest such as the separation of elements into sulphide and silicate phases, geochemical coherence, behaviour of elements in fractionated silicate minerals, melting points of olivine and of Ge and Ga substituted feldspars, anion affinity and structure, and the ability of elements to form complexes, are discussed. Attempts at interpretation are made on the basis of the valence, size and anion affinity of cations and the polarizability of the anions.

INTRODUCTION

Mainly as a result of the pioneering work of the late V. M. GOLDSCHMIDT and of others, it has been possible to interpret many geochemical properties of elements largely on the basis of ionic charge and size. In general, one may state, for example, that ions of elements which carry the same formal charge and which have similar ionic radii, frequently show like chemical and crystal-chemical properties, and as a result they are likely to be closely associated in nature. Such a generalization has for the most part been borne out by experimental evidence and several examples of closely associated groups of elements have been found; for example:

$$Zr^{4+}\ (0{\cdot}79\ \text{Å}) - Hf^{4+}\ (0{\cdot}79\ \text{Å})$$
$$Ga^{3+}\ (0{\cdot}62\ \text{Å}) - Al^{3+}\ (0{\cdot}51\ \text{Å})$$
$$K^{+}\ (1{\cdot}33\ \text{Å}) - Rb^{+}\ (1{\cdot}47\ \text{Å}) - Tl^{+}\ (1{\cdot}47\ \text{Å})$$
$$Nb^{5+}\ (0{\cdot}69\ \text{Å}) - Ta^{5+}\ (0{\cdot}68\ \text{Å}),$$

several rare earths, and others. Yet, the closeness of their association is much a matter of degree and cannot be assessed by radius and charge alone whether we regard their distribution in oxides and silicates (bond to oxygen), in sulphides (bonded to sulphur) or in both phases. Moreover, some pairs, for example, Mg^{2+} (0·66 Å) — Ni^{2+} (0·69 Å) show only a moderately close association, whereas for a few, Cu^{+} (0·96 Å) — Na^{+} (0·97 Å) and Sr^{2+} (1·12 Å) — Hg^{2+} (1·12 Å), there is virtually no geochemical association; in fact, there is hardly any chemical resemblance at all between these pairs other than the fact that SrF_2 and HgF_2 both have the ionic fluorite structure. Clearly then there are other properties which are also important for determining the closeness of geochemical association, a fact about which geochemists have been fully aware for some time.

Other questions also arise which cannot be interpreted by considerations of valence and size alone; for example, the unique ability of nickel to enrich in the earliest mafic minerals in a differentiated rock sequence as at Skaergaard (Wager and Mitchell [1]). Then there is the problem of whether or not to use *ionic* radii in sulphide minerals, where it is usually accepted that bonding is dominantly covalent and which immediately implies a sharing of electrons with the partner and a crystal structure which is not determined by a packing of spherical ions of definite size but by other considerations.

The main object of this paper, the second on ionization potentials, is to use the ionization potential as an aid for interpreting and understanding such problems as those noted above, as well as of others of geochemical interest.

Nature of the Chemical Bond and the Mechanism of its Formation

In order to attempt an interpretation of geochemical and chemical properties, a stand must be taken with regard to one's conception of the chemical bond. This discussion is limited to metal-nonmetal compounds. It is no understatement to say that ideas about the mechanism of bond formation and the nature of the bond itself, particularly its physical reality, are in turmoil. Although all agree that the bonds between such elements as potassium and chlorine in a crystal of KCl are essentially ionic, serious disagreement develops when compounds are considered in which the bonding shows a significant proportion of covalent character. Although there is an agreement that bonds in CuCl, (as compared with KCl) and in sulphide minerals, are dominantly non-ionic and that in borates, silicates and certain other compounds, bonds might be *described* as "aproximately half covalent and half ionic" real disagreement arises when the actual nature and mechanism of formation of these bonds are considered. This problem will be discussed from two approaches —(1) Covalent, and (2) Ionic. Discussions are brief and are given mainly to emphasize differences in underlying philosophy.

Covalent approach to bond formation

Following Lewis [2] it has become common to regard a covalent (homopolar or electron-pair) bond as a sharing of electrons between partners, in the process of which an octet of electrons is a goal (octets are quite often exceeded, as in IF_7, SF_6, PF_5, OsF_8, for example, and in several complex ions). Subsequent wave mechanical treatment (see, for example, Pauling [3]) of the covalent bond offers an explanation for the need for two electrons for the formation of each bond by requiring that the spins of the two bond-forming electrons be paired. Exchange forces, an outcome of wave mechanical treatment, are considered to hold elements together in a covalent bond; no example exists of exchange forces in classical physics. An outstanding feature of the development of a wave mechanical approach to the covalent bond has been the ability to predict certain spatial dispositions of bonds; for example, a tetrahedral disposition in diamond (Slater [4], Pauling [5]) and a square coplanar disposition in many compounds of divalent palladium, platinum, copper, silver and sometimes nickel. For such purposes hybridization of bond orbitals has been necessary and this approach has been applied extensively though not always successfully. For a discussion of this topic, see Wells [6].

Although covalent bond theory was developed to apply essentially to a pure covalent bond, it was realized that various gradations between the two extremes, ionic and covalent, were to be found. PAULING [3] has utilized the concept of resonance as an aid in interpreting bond properties*. Thus, bonds in the tetrahehral ions PO_4^{3-}, ClO_4^-, and in the planar (triangular) ions BO_3^{3-}, CO_3^{2-} and NO_3^- are quite often *approached* as if they were covalent, but various resonating valence structures (single-bond covalent, double-bond covalent and ionic) are introduced (see, for example, PAULING [3]) to account for bond length discrepancies from those predicted from covalent radii sums. It should be remembered that bonding in these ions is not much different from Si-O bonds in various silicates. Sometimes a distinction is made between bonding in the above ions, the structures of which are in conformity with the ionic radius ratio rules, and those "covalent" compounds such as CuCl, ZnO and most sulphide minerals which have structures that do not conform with the ionic radius rules.

The extent to which various resonance features have been applied is well exemplified by a comprehensive discussion by WELLS [7] of bond-lengths in various molecules and ions. Despite the use of various resonance structures and an electronegativity correction (STEVENSON and SCHOMAKER [8]), WELLS is forced to conclude that no satisfactory explanation can be given of bond length discrepancies when using the information now available. When we examine various trends in properties and of bond type found in geological materials, the situation seems far worse, and attempts at interpretation on the basis of a covalent approach, whether we invoke resonance or not, appear to make little headway. (It should be recalled that resonance theory invokes the use of limiting structures which by admission have no existence in reality.) The use of electronegativity (see below) alleviates the position a little, but does not appear as effective as that of the alternative ionic approach for interpreting various chemical and geochemical problems involving a metal-nonmetal bond. Despite, therefore, the tremendous effort that has gone into the covalent approach of the chemical bond, particularly during the past two decades, its success in organic chemistry and its ability sometimes to predict the spatial disposition of bonds, one is frequently left with the gravest of misgivings because of the difficulty of reconciling some of its concepts with physical reality and because it seems incapable of satisfactorily interpreting metal-nonmetal bond property trends and several other details in inorganic chemistry and geochemistry.

Before proceeding to an alternative approach to the nature and mechanism of formation of bonds, some comments will be made on electronegativity. This quantity has been developed mainly by PAULING [3] to indicate bond type, namely, degree of ionic or covalent character in a bond. It is defined as the power of a neutral atom in a stable molecule to attract an electron unto itself. MULLIKEN [9], [10] has suggested that the average of the *first* ionization potential and the electron affinity of an atom should be a measure of its electronegativity. As electronegativity refers to stable equilibrium conditions, it is not used to indicate the mechanism of bond formation. Its use in geochemical problems has been discussed by

* Electronegativity has been used to indicate degree of ionic or covalent character of the bond, but inasmuch as this property as such is not involved in the underlying philosophy of the covalent approach to bonds, it is discussed separately later.

Ramberg [11] who has found it useful as an aid for distinguishing bond types in minerals; see also Fyfe [12] and Gruner [13].

The ionic approach to bond formation

In the ionic approach to bond formation use is made of the concept of polarizability (deformability) of ions as outlined by Fajans and Joos [14] and Fajans [15], [16] and applied to crystal chemistry by Goldschmidt [17] and by others. For a recent discussion on the use of this concept, see Förland and Weyl [18], for example. This theory will be considered to apply to all metal-nonmetal compounds irrespective of whether bonding is almost purely ionic, as in a KCl crystal, for example, or whether it is mainly non-ionic (covalent) as in CuCl, for example. For the time being, at least, the ionic approach won't be regarded as applying to compounds of the lightest elements (NO, CO, for example) nor to molecules of the type Cl_2, N_2, and O_2. Although we are, of course, concerned here mainly with the solid state, and consequently won't discuss bond properties of vapour molecules, the mechanism of bond formation to be discussed will be regarded as taking place irrespective of whether the product is a gas or a solid. At this stage it should be pointed out that in problems in which the nature of bonds is discussed, almost all attention is usually focussed on the properties of the bond in the product of the reaction and little, if any, on the mechanism of the bondforming reaction. It is felt that at least equal emphasis should be placed on the mechanism of bond formation, and the various geochemical problems involving properties of bonds will be approached in this spirit.

The formation of a bond via the ionic approach will be considered to pass through three main stages; first, that of initiation of the reaction, second, an intermediate or transitory "free-ion" stage, and third, equilibrium. For the sake of discussion, copper and sodium will be regarded as the metals, and chlorine as the nonmetal partner.

Consider contact between a metal atom and one of a nonmetal. As a consequence of some interpenetration of their electronic systems their outermost electrons are exposed to two competing forces of attraction. As the electron affinity of the nonmetal is usually much greater than that of the metal atom, the reaction will be considered to be initiated by this difference in electron affinities which tends to cause a transfer of an electron from the metal to the nonmetal thereby forming an anion and a cation. It is not quite clear why electron affinities of nonmetals are greater than those of metals. The intensity of the electrostatic force of attraction (field) on the outermost part of the respective atoms may be one major factor, and the *actual* cause for the reaction may be mainly, but not entirely, due to exposure of outermost electrons to a field difference. First ionization potentials may be used as a guide to indicate relative field strengths. In nonmetals, first ionization potentials range from 17·42 v for fluorine to about 10 v, and for metals, from 9·2 v for gold to 3·9 v for cesium. For sodium and copper first ionization potentials are 5·12 and 7·7 v respectively, whereas that of chlorine is 12·96 v.

The formation of a cation and an anion closes the first stage. It is understood, of course, that cation does not necessarily mean a singly charged cation but refers to any given stable state; for example, for silicon it would be Si^{4+}. Whether an element forms singly, doubly, trebly, or a more highly charged cation, depends to some considerable extent on ionization potential differences; that is, difference

between first and second, second and third, third and fourth, and so on. The use of ionization potentials to indicate stable valence states won't be discussed in detail here but is referred to again later in the discussion on ionization potentials and stable valence states.

The cation-anion relationship will be regarded as a transitory, intermediate stage in which the properties of the cation and anion are virtually those of free ions; *anion affinity** will be defined as the power of a free cation to attract anions. In contrast to electronegativity which is defined as referring to equilibrium conditions in a molecule, anion affinity refers to a transitory free ion relationship. It should not be confused with chemical and geochemical affinity. The ionization potential, first for univalent ions, second for divalent ions, and so on—see Table 2 in Part 1 on the use of ionization potentials—will be used to *indicate* anion affinity. Thus, for example, when we say that the third ionization potential of gallium is 30·7 v and that of aluminium is 28·4 v, we are informed of two facts; first that the amount of nuclear screening is less in gallium than in aluminium, and second, that as a consequence when Ga^{3+} and Al^{3+} are formed, the force of attraction (anion affinity) associated with Ga^{3+} will be slightly, but definitely, greater than that of Al^{3+}. Polarizing power, as defined by GOLDSCHMIDT [17] as Z/r^2, the ionic potential Z/r of CARTLEDGE [19] and field strength (DIETZEL [20]) are related properties; none of these, however, take into consideration variable screening of the nucleus by ions of different electronic configuration.

When dealing specifically with the polarization-deformation of the anion in the field of the cation, ionization potentials will be used in exactly the same way as anion affinity, which is merely a general term.

Coulombic attraction between cation and anion draws them together to give a final equilibrium product. If the anion affinity is small (Na^+, for example) the Na^+-Cl^- bond will be essentially, though not perfectly ionic, provided the product is a crystal. If the anion affinity is great, Cu^+, for example, the anion may be strongly polarized or deformed in the process of which its negative charge distribution is drawn toward the cation; there may or may not be overlapping of their respective electronic systems and the degree of covalent character may be regarded as the degree with which the anion is polarized. The electronic system of the cation may also be deformed in the process of bond formation, but usually the anion will be polarized to a far greater extent. Although an overlap or sharing of electronic systems is envisioned in the bond of dominantly covalent character, actual sharing of an electron pair as usually understood in the covalent approach is not necessarily implied, nor an insistence that an octet of electrons be attained, although this is usually attained in any case. We will also have to assume that by strongly polarizing the anion it will not be capable of showing anion-anion repulsion.

It has been stated (GLASSTONE [21]) that because of the large amount of energy required to produce small highly-charged ions such as S^{6+}, N^{5+}, Si^{4+}, B^{3+}, it is doubtful whether such ions could be formed in chemical formation. It is, however, not the ionization energy but differences between first and second, second and third, and so on, which should determine the degree of ionization. Thus for silicon, the

* Mrs. V. Ross of the Dept. of Geology, M.I.T., has suggested the use of effective nuclear charge. This has some advantages but for the time being at least, the use of the term anion affinity will be retained.

first, second, third, fourth and fifth ionization potentials are 8·15, 16·34, 33·5, 45·13 and 166·5 v respectively. Ionization can apparently proceed quite easily from $Si^{+} \rightarrow Si^{2+} \rightarrow Si^{3+} \rightarrow Si^{4+}$, because ionization potential differences are not large (maximum 17 v) but is held up at Si^{4+} because the difference between fourth and fifth ionization potentials is excessive (121 v) and consequently no quinquivalent silicon compounds are known. The fifth electron is particularly difficult to remove because it is from the complete L shell.

Although the description given above of the mechanism of bond formation is a brief outline and is undoubtedly an oversimplification of the true state of affairs, it is merely given to serve as a working basis for the problems at hand. At the outset it must be pointed out that at present the ionic approach suffers from one weakness —its inability to predict the spatial disposition of bonds in crystals which are structurally non-ionic. As will be shown later, however, regularities between anion affinity and structural changes do exist, but it is difficult to assess their importance.

The mechanism of bond formation has been discussed as if it were a reaction between neutral atoms. Naturally, in geological materials one is rarely dealing with neutral atoms. Whether we regard, say, crystallization from a melt or some reaction in water, it makes little difference. For example, most metals ionize in water because it is a strong dielectric and if H_2S is passed into a solution of heavy metals (Ni, Pb, Cu, Zn, etc.) their precipitation as essentially covalent compounds may be regarded as having been preceded by a reaction between S^{2-} and the respective cations. Actually, the cations will be hydrated and the first stage in this reaction would involve a removal of the envelope of surrounding water dipoles from the effective field of the cation, followed by the reaction of S^{2-} and cation.

A most important assumption in the ionic approach used here is that irrespective of whether reaction takes place in solution, melt, or solid, and irrespective of how we wish to describe the bonds in the resultant equilibrium product, the history of each metal-nonmetal reaction involves at some stage a transitory state in which the properties of free ions play a dominant role in determining the bond properties of the product. Nonmetals includes organic radicals as in organometallic compounds and product may be a simple compound or may refer to a bond in a complex such as that of Pd-Cl in $PdCl_4^{2-}$.

Discussions of Various Topics of Geochemical Interest

1. *Separation of elements into silicate, sulphide and metal phases*

Goldschmidt [22] has suggested an empirical geochemical classification of elements into three main solid phases—metal, sulphide, and oxide + silicate—and this serves as a useful starting point for any geochemical discussion. Neumann [23] points out that measured tendencies of elements to form certain bond types should be valuable in providing a theoretical basis for the empirical classification given above: the discussion here attempts an interpretation on this basis. Attention is given mainly to the sulphide and oxide phases.

The anionic partners in question, O^{2-} and S^{2-}, have significantly different properties. Not only is S^{2-} larger than O^{2-} (respective radii, 1·85 Å and 1·40 Å), but S^{2-} is polarized much more easily than O^{2-}. As a consequence a bond between sulphur and a given metal has a greater degree of covalent character than one between

oxygen and the same metal and the immiscibility of oxide + silicate and sulphide phases may be attributed to some considerable extent to the high degree of covalent character of the bonds in sulphide minerals. It follows therefore that for ions of the same valence * and similar size, those with the highest value of I should show the greatest tendency to form covalent bonds with sulphur and hence appear in the sulphide phase. In the comparisons below, ions are grouped according to valence and size. Ideal comparisons are only possible when both valence and radii are equal; for example, Zr^{4+} and Hf^{4+}. For many purposes, however, grouping according to size magnitude is satisfactory, although radii differences must be taken into account in a detailed discussion.

Univalent elements

Table 1 shows univalent ions arranged in order of increasing anion affinity.

Table 1. Univalent cations

	Cs^+	Rb^+	K^+	Na^+	Li^+	Tl^+	Ag^+	Cu^+	Au^+
I (volts)	3·9	4·2	4·34	5·14	5·4	6·1	7·57	7·7	9·22
Radius (Å)	1·67	1·47	1·33	0·97	0·68	1·47	1·26	0·96	1·37

I increases ⟶

Univalent cations require an I value of some 6 v before they form with sulphur a bond of sufficiently high degree of covalent character which will enable them to be accepted into the covalent sulphide phase. Thallium and elements on its right are chalcophile (sulphophile). The dividing line is drawn through thallium because in many respects thallium is a borderline element showing some geochemical and chemical properties very similar to its nearest large neighbours, K^+, Rb^+, and Ag^+. For several purposes of comparison Li^+ in particular and sometimes Na^+ and Cu^+ should be omitted; the most satisfactory progression in general chemical an geochemical properties is observed by comparing only the largest cations Rb^+, K^+; Tl^+; Ag^+; and Au^+.

Mercury has the highest first ionization potential (10·43 v) of any "metal". Mercurous mercury is, however, di-atomic and it is difficult to compare the behaviour of Hg_2^{2+} with other univalent cations. The fact that mercurous mercury is di-atomic may of course in part be due to the extremely high value of its ionization potential.

Divalent cations

Divalent ions are separated into two size groups. The division is arbitrary but is based in part on the fact that the 6:3 rutile structure is common to fluorides of the mediumsized group, whereas the 8:4 fluoride structure prevails in fluorides of the large-sized ions.

Table 2 (a) and (b) shows divalent ions arranged in order of increasing anion affinity.

* Valence will be used here in place of *charge* so that no confusion arises as to whether actual or effective nuclear charge is meant; it will be recalled that anion affinity is closely related to effective nuclear charge.

Table 2.

(a) *Medium-sized (0·6–0·89 Å) divalent cations*

	Mg^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Zn^{2+}	Ni^{2+}	Pt^{2+}	Pd^{2+}	Cu^{2+}	Ag^{2+}
I (volts)	15·03	15·64	16·24	17·4	17·95	18·2	19·3	19·9	20·3	22
Radius (Å)	0·66	0·80	0·74	0·73	0·74	0·69	0·80	0·80	0·72	0·89

I increases ⟶

(b) *Large (0·95–1·35 Å) divalent cations*

	Ba^{2+}	Sr^{2+}	Ca^{2+}	Pb^{2+}	Cd^{2+}	Hg^{2+}
I (volts)	10·0	11·03	11·9	15·05	16·9	18·8
Radius (Å) . . .	1·34	1·12	0·99	1·20	0·97	1·10

I increases ⟶

For medium-sized (0·6–0·8 Å) cations, an *I* value of some 15·5 v or more is required before the element is able to enter the sulphide phase. Manganese occupies an interesting intermediate position in bond-forming properties in much the same way as does thallium in the univalent group. It is of considerable interest to observe that although manganese is an abundant element it does not form magmatic sulphide minerals of its own. Most manganese enters the silicate minerals, but its *I* value is just sufficient to enable it to be accepted into sulphide minerals such as pyrite, sphalerite, etc. All elements on the right of manganese enter sulphide minerals. In nature, silver is always univalent (see discussion No. 8) but the unique location of Ag^{2+} on the farthest right is of particular chemical interest because Ag^{2+} has the greatest *I* value of any divalent cation.

For large divalent ions (0·95–1·35 Å) the dividing line is probably somewhat less than 15 v. Lead and all elements on its right are typically sulphophile.

Although tin is usually quadrivalent, the divalent state is sometimes present (radius of Sn^{2+} = 0·93 Å) and the presence of tin in some sulphides is probably due to SnS. Likewise, germanium and gallium may be present in sulphides in the divalent state. Respective *I* values for Sn^{2+}, Ge^{2+} and Ga^{2+} are 14·63, 15·93 and 20·51 v.

When trivalent cations of the size range, 0·74 to 0·96 Å, are examined (Table 3), regularities are again present, although they are not quite so well developed as with mono- and divalent cations.

Table 3. Trivalent cations

	Y^{3+}	Sc^{3+}	Sb^{3+}	Bi^{3+}	V^{3+}	In^{3+}
I (volts)	20·5	24·75	24·83	25·56	~26·5	28·03
Radius (Å) . . .	0·92	0·81	0·74	0·96	0·76	0·81

I increases ⟶

If pairs of ions of almost identical radius and large I difference are considered, their relationship is as would be anticipated. For example, in the pair $Sc^{3+} - In^{3+}$, only indium is characteristically enriched in sulphide minerals; Y^{3+} and Bi^{3+} show about the same relationship as the pair $Sc^{3+} - In^{3+}$. In general, an I value of some 24·8–25·0 v is required before an element enters the sulphide phase, and antimony and elements on its right may be found in sulphide minerals. The location of vanadium does, however, not appear to be accurate and although vanadium is found in sulphides (Noddack and Noddack [24] report 0·004 % in primary magmatic sulphides) this element is not as chalcophilic as its I value would tend to indicate. It is probable of course that other properties such as the polarizability of the cation and a non spherical charge distribution even in the free ion must play some role; these properties become increasingly important when the I difference, expressed as a ratio (see discussion No. 2) is small. If, for example, Sb^{3+} and Bi^{3+} were more easily polarized than V^{3+}, this would tend to increase their tendency to form a covalent type bond.

For all valence groups, extremely high I values indicate that the outer valence electrons are tightly held. As a result they are reluctant to enter into chemical combination and elements with very high I values should tend to remain native. Gold has by far the highest I value of the univalent elements and is by far the most noble and typically siderophilic element of the group. Copper and silver also have well developed siderophilic tendencies whereas thallium is invariably combined. Reference to Fig. 1 in Part 1 on the use of ionization potentials, shows that entry of $4f$ electrons causes an elevation in ionization potentials of the 18-electron elements in the sequence $Au^{+} \rightarrow At^{7+}$; the effect is most pronounced in gold and decreases regularly in this sequence as the inverse square relationship between I and r restores itself (see Part 1). Were it not for this effect, gold would not have been so characteristically inert and univalent gold would have had chemical and geochemical properties midway between univalent silver and thallium; for the same reason mercury would have been more reactive and would probably have had properties similar to divalent lead.

According to the I value, the order of increasing siderophilic tendency in the medium-sized group should be Mg, Mn, Fe, Co, Zn, Ni, Pt and Pd. Copper is not included because it has a stable univalent state and is referred to above. With the exception of zinc the sequence appears to accord exactly with observation, platinum and palladium being characteristically noble with nickel less so, but nevertheless showing a well developed siderophilic tendency, followed by cobalt and iron. The fact that zinc is not as siderophilic as say, cobalt, may in part be due to the fact that abundant iron readily accepts cobalt in solid solution. If therefore we use meteorite data as a basis for measuring siderophilic tendencies, the fact that the metal phase is dominantly iron should not be overlooked. In the large-sized divalent group, mercury has by far the largest I value and this element is the most noble of the group.

When dealing with an aqueous environment, as in the sedimentary cycle, oxidation potentials may be used to indicate the likelihood of a metal occurring in the native state (Mason [25]). Ionization potentials are also instructive for this purpose but because of such effects as hydration and formation of complexes, they are not as satisfactory as oxidation potentials.

2. *Association of elements (geochemical coherence)*

If anion affinity is important for determining the general chemical and geochemical properties of elements, it follows that elements which have ions of equal valence and similar radius should be closely associated in nature provided they have similar I values; moreover, it would not be unreasonable to expect that the anion affinity difference between a pair or more of ions should provide a measure of their closeness of association (geochemical coherence).

Before proceeding any further it will be necessary to define some basis on which comparisons of geochemical coherence will be made. For a start, unusual environments should be avoided as much as possible, and the following is a suggested classification of categories which will be used here for examining the geochemical coherence of a pair or more of elements.

1. Phase behaviour (sulphide-silicate).

2. Association in common igneous rock types. Ultramafics. Intermediate types. Granite and associated types.

3. Association in pegmatites and related dyke-like bodies.

4. Association during the sedimentary cycle.

5. Unusual environments—used only to illustrate detail.

This, of course, is purely arbitrary and may be modified to suit any particular study of geochemical coherence. The metal phase should be included, but for our present purpose which does not concern the metallic bond, it will be excluded.

The discussion which follows is general, but various aspects are taken up in detail in later discussions.

Table 4. I, r and φ values for various pairs of ions

		I	r	φ
1^+	K	4·34	1·33	1·04
	Rb	4·18	1·47	
1^+	Tl	6·11	1·47	1·45
	Rb	4·18	1·47	
1^+	Cu	7·72	0·95	1·50
	Na	5·14	0·97	
2^+	Ni	18·20	0·69	1·20
	Mg	15·03	0·66	
2^+	Ca	11·9	0·99	1·42
	Cd	16·9	0·97	
2^+	Hg	18·75	1·12	1·70
	Sr	11·03	1·12	
3^+	Ga	30·7	0·62	1·08
	Al	28·44	0·51	
3^+	In	28·03	0·81	1·15
	Sc	24·80	0·81	
4^+	Ge	45·7	0·53	1·01
	Si	45·1	0·42	
4^+	Zr	34·0	0·79	1·08
	Hf	31·0	0·79	
5^+	Nb	52·0	0·69	1·16
	Ta	44·8	0·68	

Table 4 gives I values for each of the various pairs of elements referred to in the introduction as well as a few others. In addition, the value of the ratio $I_a/I_b = \varphi$, of two ions a and b and referred to hereafter as the anion affinity index, is given because it is frequently more instructive to use the ratio rather than differences in absolute values. In each example in Table 4, the ion of greater anion affinity is made the numerator. Ionic radii are included in Table 4.

K—Rb

As would be anticipated, geochemical coherence is high. Neither element is detectable in sulphide minerals and statistical investigations, part in the press (Ahrens,

Pinson and Kearns [26]) and part in preparation, show that throughout the main igneous rock types, geochemical coherence is developed to a much greater extent than has usually been thought. In pegmatites, however, coherence is only moderate because of the characteristic tendency of rubidium to enrich relative to potassium in late phase replacement-crystallization. This behaviour is undoubtedly due to a significant difference of 12% in radius and not to the small 4% difference in I. Throughout the sedimentary cycle, coherence remains very well developed as shown by some hundreds of rubidium and potassium determinations in various sediments, mainly shales, sandstone and quartzite (Canney [27]); unpublished data on deep sea cores likewise show a vary close association of potassium and rubidium. The K—Rb association may be disturbed in the presence of much organic matter (Canney [27] and Eugster [28]).

Rb—Tl

Thallium alone is concentrated in sulphides, because of its considerably greater anion affinity. In silicates, however, coherence appears to be greater (see Ahrens [29] for example) than would be anticipated from a value of $\varphi = 1{\cdot}45$; this appears to be the only example of unexpected behaviour. It is possible that the above value of I should be given greater consideration than φ in this case because 6·1 v may not be significantly different, *with regard to* O^{2-}, than 4·1 v. However, whether we regard this as an actual anomaly or not, it should be recalled that in almost every other general chemical and geochemical respect the behaviour of Tl^{+} is exactly as anticipated from its I value and that in the sequence K + Rb; Tl; Ag; Au, thallium is accurately placed. Coherence in the sedimentary cycle is not developed (see, for example, results and discussion by Canney [27]) and apparently the difference in I is able to assert itself.

Cu—Na

As would be expected, geochemical coherence is feeble in every respect.

Ni—Mg

Nickel alone is chalcophile. In common silicate rocks and minerals the Ni—Mg coherence is moderate but nickel shows a characteristic tendency to enrich in the earliest ferro-magnesians; see, for example, Wager and Mitchell [1], and discussion No. 3. Coherence in the sedimentary cycle is poor and in general geochemical coherence is not well developed, which is in accordance with a moderately large value of φ.

Hg—Sr

In accordance with a very large value of φ this pair apparently shows no geochemical coherence whatsoever.

Ga—Al

Ga alone shows chalcophilic tendencies, but this is quite likely due to its presence in sulphides in the divalent state. This, of course, introduces a complication in a discussion of this type, namely, variable valence. If, however, we confine ourselves to the particular valence states in question, gallium and aluminium are extremely closely associated, as would be expected from the small value of φ. Early observations

by Goldschmidt and Peters [30] indicated a marked enrichment of gallium relative to aluminium when passing from ultramafics to granite. Later observations by Nockolds and Mitchell [31] and Wager and Mitchell [1] indicate, however, that the ratio Ga/Al remains almost constant and increases only slightly in fractionated rock sequences and in accordance with this, a statistical examination of the Ga/Al ratio in many North American rocks [32] shows that the Ga/Al ratio is remarkably uniform. Data for the sedimentary cycle are fragmentary, but a high degree of coherence appears to be maintained. An investigation by Bell [33] shows that in late phase crystallization in pegmatites some gallium enrichment is found as in amazonite and lepidolite; this is not marked and is not nearly as well developed as the enrichment of rubidium relative to potassium. Rankama [34] has discussed geochemical coherence and concludes that the coherence of Ga—Al is not particularly well developed. However, this conclusion was based in part on the observations of Goldschmidt and Peters [30] who not only reported that the ratio Ga/Al increased sharply as noted above, but that the ratio Ga/Al in opalized wood was much different from magnitudes found in igneous rocks. Opalized wood is, however, an unusual environment and in order to compare the geochemical coherence of gallium and aluminium with other pairs of elements, they too should be determined in a similar environment.

In—Sc

In^{3+} and Sc^{3+} are identical in size, yet coherence is hardly better than moderate. Indium alone enters the sulphide phase because of its considerably greater I value. Shaw [35] has recently discussed the geochemistry of indium and shows that the concentration of this element varies considerably in many of the common igneous rock types; this is apparently due in part at least to the presence or otherwise of sulphide minerals. Scandium and indium are geochemically similar insofar as they both show a well developed tendency to replace Fe^{2+} and Mg^{2+} in pyroxene, emphibole and mica but not in olivine.

Ge—Si

Germanium alone is sometimes found in sulphides but this may be due to variable valence (presence of Ge^{2+}); otherwise, as would be expected from the value of q, germanium und silicon appear to have a high degree of geochemical coherence. Unfortunately, a large number of accurate germanium determinations in many rock types is not at hand. There appears to be some enrichment of germanium relative to silicon in some pegmatitic minerals, but this is almost certainly due to a considerable difference in radius (25%) and not to a small difference in I.

Zr—Hf

Both are characteristically lithophile, and geochemical coherence is well developed in all categories, which accords with the small value of φ. The properties of this pair provide one of the most satisfactory tests of the significance of I for determining general geochemical and chemical properties. Not only are valence and size identical, but electronic configurations are the same, and consequently other possible factors such as differences in the polarizability of the *cation* need not be taken into con sideration. Two real differences in properties are first, the greater ability of

Zr^{4+} to form complexes (see discussion No. 7) and the greater basicity of HfO_2; both differences are anticipated from the fact that Zr^{4+} has a greater anion affinity. The difference in basicity is important for understanding their geochemical association.

In the pair Ga—Al, $\varphi = 1{\cdot}08$ and $Ga(OH)_3$ is the weaker base and in this particular respect the relationship of gallium to aluminium is very similar to that of zirconium to hafnium.

Nb—Ta

In a general way, the association of this pair may be compared with that of zirconium and hafnium except that in almost every respect geochemical coherence is distinctly weaker, which accords with a greater value of φ (1·16). The comments above on the value of the comparison of zirconium and hafnium apply equally well to the pair Nb—Ta. See RANKAMA [36], [37] for a detailed account of the geochemistry of tantalum and niobium and their association.

Other examples such as Cd^{2+} and Ca^{2+} ($\varphi = 1{\cdot}42$; possible slight coherence), K^+ and Au^+ ($\varphi = 2{\cdot}1$; no coherence), some rare earth pairs (φ close to unity; very well developed coherence in all respects), support the general conclusion which may now be made from the above discussion, namely, that for geochemical coherence to be close in all respects, ΔI and Δr must each be less than about 10%. Only zirconium and hafnium and a few rare earth pairs appear to qualify in every respect. Other pairs may show well developed geochemical coherence in many respects, but either the radius difference is significant under certain conditions (for example, rubidium and potassium in pegmatites) or the I difference is significant (for example, rubidium and thallium in phase separation). It does not necessarily follow that a pair of elements must be closely associated if ΔI and Δr are less than 10%; other properties such as the polarizability of the cation may play a role. Unfortunately very little is known about the polarizability of cations.

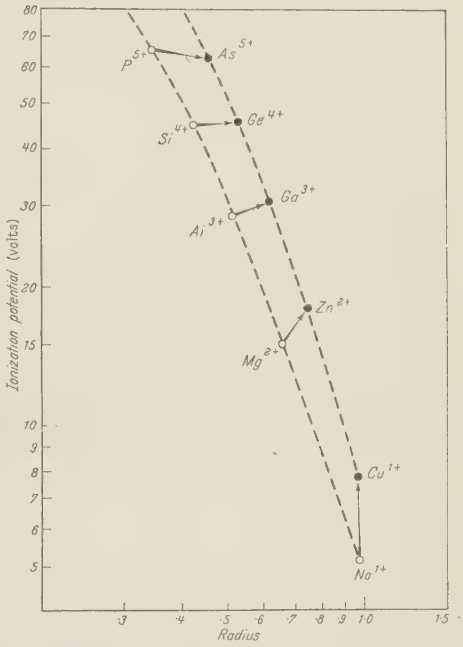

Fig. 1. The radius—ionization potential relationship between pairs of 8 and 18 electron ions is seen to vary regularly with change in nuclear charge.

Progressive changes in the geochemical relationship between pairs of elements of like valence but different electronic configuration may be most instructively shown when depicted graphically. Fig. 1 shows a plot of r vs I (log-log co-ordinates) for 1^+, 2^+, 3^+, 4^+ and 5^+ ions from the 8 and 18-electron sequences, $Na^+ \rightarrow Cl^{7+}$ and $Cu^+ \rightarrow Br^{7+}$. The degree of geochemical coherence and various observed regularities in property changes are in almost quantitative accordance with the plotted trends of I and r in Fig. 1.

The various reasons why the difference in anion affinity must be small in order for geochemical coherence to develop will become apparent in subsequent discussions: one example, that of the separation of elements into phases, has already been discussed (discussion No. 1).

3. Relationship of ions of equal valence and like size during fractionation of silicates

It is not quite clear which stage in the history of formation of a crystal is most significant for a discussion of this type. The stage at which a significant degree of polymerization of SiO_4 tetrahedra first develops, for example, could be regarded as most appropriate for some purposes, but the following rule will be stated as if it applied to a growing crystal and will be used as a basis of the discussion under this heading. This rule states that:

Table 5. I, r, and F values for medium-sized divalent ions

Ion	*I*	*r*	*F*
Cu^{2+}	20·3	0·72	28·2
Ni^{2+}	18·2	0·69	26·4
Pd^{2+}	~19·9	~0·80	~25·0
Zn^{2+}	17·95	0·74	24·4
Co^{2+}	17·4	0·72	24·2
Mg^{2+}	15·03	0·66	22·8
Fe^{2+}	16·24	0·74	22·0
Mn^{2+}	15·64	0·80	19·5

When two ions of the same valence and equal or similar radii compete for a given structure site in a growing crystal, the one with the greater electric intensity (field) should arrive first.

Whether it remains as a permanent occupant of the site or not is another matter. This rule though related, is distinctly different from one given by Goldschmidt [22] which states that the smaller of two ions of similar size and equal valence is preferentially accepted, because the length of its bond is shorter and consequently should be stronger (see, for example, Goldschmidt's [22] discussion on olivines). We shall see presently, however, in this discussion and in discussion No. 4, that bond strength depends mainly on the nature of the bond and to a much smaller extent on length unless extremes are involved.

At this point it will be necessary to define what is meant by field, as distinct from anion affinity. Whereas anion affinity and polarizing power are properties which are regarded as associated with the surface area of the ion as a whole, electric intensity does not have dimensions of area and the relationship I/r, in volts/A will be used to indicate field. As it is not actually equal to the ionic field, the term field function (F) will be used. Naturally when making comparisons of ions of equal or almost equal radii, nothing is gained by using F in place of I. The migration energy of a cation, as defined by Wickman [38] is related to F and also to I.

Consider medium-sized divalent ions (Mg^{2+}, Fe^{2+}, etc.); I, r, and F values are given in Table 5, in order of decreasing F.

According to the above rule the proportion of early to late arrivals should be heavily in favour of Cu^{2+}, Ni^{2+}, and Pd^{2+}. However, whether these ions will be rejected* or not should depend largely on two considerations: (1) the stability of

* The possible importance of ionization potentials on the ability of one cation to replace another has been discussed by Rankama and Sahama ([39], p. 123). They show that although exceptions exist, greater freedom of substitution is to be found in pairs of ions which have a small I difference; no interpretation is given.

the bond between them and the partner, in this discussion O^{2-} in a silicate, and, (2) their stereochemical bond disposition toward O^{2-} under these particular conditions.

Ions with extreme I values are apparently capable of deforming O^{2-} to such an extent that the bond is either weak or completely unstable. It is, of course, extremely difficult to determine the stability of a metal-O bond in silicates, but the following data on heats of formation (ΔH) are instructive.

Table 6 gives ΔH values (Kcal/mole) for several hypothetical feldspars (data from Rankama and Sahama [39], p. 139).

Table 6. ΔH values in Kcal/mole for several hypothetical feldspars

K *feldspar type*				*Plagioclase type*			
	r	I	ΔH		r	I	ΔH
K^+	1·33	4·34	—117	Sr^{2+}	1·12	11·03	—92
Tl^+	1·47	6·1	— 46	Ca^{2+}	0·99	11·90	—61
Ag^+	1·26	7·57	+126	Pb^{2+}	1·20	15·04	—34
Au^+	1·37	9·2	~+135	Cd^{2+}	0·97	16·9	+41
				Hg^{2+}	1·10	18·8	~+70

In each series, the radius of the large cation may be regarded as approximately constant and satisfies the radius ratio requirements for high co-ordination.

Negative ΔH values are supposed to indicate that a feldspar is stable, whereas a positive value indicates instability. The regular decrease in stability with increase in I may be attributed to a progressive weakening of the bond as a result of increased polarization of O^{2-}. The Au—O and Hg—O bonds in particular must be extremely weak and as a result Au^+ and Hg^{2+} may be rejected from their locations in favour of ions capable of forming stable bonds.

The same type of reasoning can presumably be applied to medium-sized divalent ions such as Cu^{2+} and Pd^{2+}.

If, for the particular environment, the stereochemical disposition of bonds about the cation does not conform with the usual cation/anion ratio rules for ionic structures, there will be a considerable tendency to reject it. Consider, for example, Cu^{2+} and Pd^{2+}. Both appear to have a tendency to assume a coplanar disposition toward oxygen under certain conditions, and for this reason they would tend to be rejected from a site in a growing crystal which is structurally ionic.

In a discussion of this sort it is imperative not only to bear in mind the polarizability of the particular anionic partner under consideration, but also the general environment of the cation. In simple compounds substitution by a large variety of ions of same valence and similar size is found in the fluorides because of the great difficulty with which F^- is deformed; CdF_2 and CaF_2, for example, are capable of perfect solid solution, whereas CaS and CdS are not. It appears also that if O^{2-} is tightly bound into a radical such as CO_3^{2-}, SO_4^{2-}, VO_4^{3-}, CrO_4^{2-} and others, the maximum polarizing effect of such cations as Zn^{2+} and Cu^{2+} is not able to assert itself fully *, with the result that 6-fold ionic co-ordination obtains and substitution is possible; for example, replacement of Fe^{2+}, Zn^{2+} and Cu^{2+} for one another in

* This effect may be compared with that of contrapolarization (Goldschmidt [17]).

carbonates. Such substitution of ions of large I differences does not readily take place in silicates. In this respect zinc is particularly interesting and its co-ordination has been discussed at length by Neumann [23]. Zinc is usually in tetrahedral co-ordination with oxygen, as for example in the oxide and in the simple silicate, willemite, whereas octahedral co-ordination is rare (for details, see Neumann [23]). The common occurrence of zinc as a minor constituent (frequently up to 0·1–0·2%) in biotite (see Bray [40] for example) and its paucity in olivine may in part be due to the fact that Zn^{2+} is able to exist in octahedral co-ordination in the biotite environment whereas such is not the case in olivine.

For the sake of further discussion, consider the observed behaviour of Ni^{2+} and Cu^{2+} in igneous rocks and minerals. Both elements are equally abundant; they have the same valence and similar radii, yet whereas the interesting behaviour of Ni^{2+} appears capable of reasonable interpretation, that of Cu^{2+} is recalcitrant. True enough, copper may be found somewhat enriched in ferromagnesian minerals, but its behaviour cannot be satisfactorily interpreted with the aid of I, F and r. It seems therefore, that although Cu^{2+} is probably the earliest of all medium-sized divalent cations to arrive at an appropriate site in a crystal growing from a melt, it tends to be rejected in part, though not wholly, for one or both the above reasons. Although almost nothing is known about the geochemistry of platinum and palladium during the differentiation of silicates, a behaviour similar to that of copper may be anticipated, particularly as platinum and palladium tend to assume a co-planar bond disposition towards oxygen under like conditions.

Medium-sized ions which are apparently acceptable in all respects are Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+} and their behaviour in fractionated silicates will be discussed on the basis of the rule outlined at the beginning of this discussion.

Consider first the two common elements iron and magnesium. Magnesium has the greater value of F and should, therefore, have some preference of entry at a structure site. However, as magnesium and iron are major constituent elements, the melting points of their respective pure compounds (fosterite and fayalite) must be taken into consideration as well. Melting point differences should depend on the respective strengths of the Mg—O and Fe—O bonds and it will be shown in discussion No. 4 that this depends mainly on I and that in accordance with observation, fosterite should have the higher melting point. In fractionated olivines, both factors, order of arrival at site and bond strength of product, favour enrichment of fosterite in the early olivines.

The enrichment of nickel in earliest ferromagnesian minerals is well marked and characteristic; see, for example, observations by Wager and Mitchell [1]. As nickel is a minor constituent, the melting point need not be taken into consideration. Goldschmidt [41] suggested that strong forces were associated with divalent nickel and stated, "These forces are not only the electrostatic forces between opposite and repulsive forces of the ions, but also van der Waals' attractive forces, polarization forces and rather important true valency or electron pair forces, especially active for instance in such materials as Ni and Cr". Goldschmidt is actually referring to equilibrium conditions in the product and although various "other" forces may be present, it seems that the dominant force—that is, during the transitory or intermediate state—is that of electrostatic attraction (anion affinity) and only this force, or rather its intensity, the relationship I/r, is considered here.

Ni^{2+} has by far the greatest F value of the acceptable ions and this appears to account for its unique enrichment in ferromagnesian minerals of earliest formation. Fractionation need not be well developed as at Skaergaard, for example, because nickel, shows the same trends in Palisade diabase [42] and even in Columbia River basalt from Oregon [32] nickel may show sharp changes when passing from flow to flow.

Sandell and Goldich [43] have drawn attention to the fact that in the large number of North American igneous rocks which they examined, the association Co:Mg is much closer than that of Co:Fe, despite the fact that the radius of Fe^{2+} is closer to that of Co^{2+} and that both have similar electron configurations. Moderately close association between cobalt, and magnesium may also be observed in Skaergaard rocks (see analyses by Wager and Mitchell [1]) and also in Caledonian rocks from Scotland (Nockolds and Mitchell [31]). The respective F values are close but that of Co^{2+} as given here appears greater than Mg^{2+}, and this should cause some slight enrichment of magnesium in later fractionates which, however, does not accord with observation. It should be recalled (Part 1 on the use of ionization potentials) that the radii of Fe^{2+}, Co^{2+}, and Ni^{2+} are based entirely on measurement, and some tolerance ($\pm 0{\cdot}02$ to $0{\cdot}03$ Å) should be allowed. When dealing, therefore, with *small* differences in F values, the accuracy with which r is known should be taken into consideration; I is usually, though not always, known accurately. Mn^{2+} has by far the smallest F value and as a result should tend to enrich relative to Mg^{2+} and Fe^{2+} in a fractionated sequence. This accords with observation, but the comparison is not rigorous, because Mn^{2+} is considerably larger than Mg^{2+} and Fe^{2+} and has, as a result, a tendency to replace Ca^{2+}.

Table 7. Some I, r and F values for trivalent cations

	r	I	F
Al^{3+}	0·51	28·7	54·0
Co^{3+}	0·63	~33·8	~53·5
Cr^{3+}	0·63	~32·1	~51·0
Ga^{3+}	0·62	30·7	49·5
Fe^{3+}	0·64	30·6	48·0

Tables 7 gives I, r and F values for some trivalent cations, arranged in order of decreasing F.

Of ions which have virtually the same radius (0·62–0·64 Å) cobalt has the greatest F value; it is doubtful, however, whether any Co^{3+} exists in igneous rocks and for this discussion this ion will be omitted. Cr^{3+} appears to have a significantly greater F value than Ga^{3+} and Fe^{3+} and in general the behaviour of Cr^{3+} in differentiated rocks is in agreement with what would be expected: the situation is, however, complicated by the fact that the solubility of chromite is extremely low in most magmas. The radius of Al^{3+} is considerably smaller than the radii of the other ions and is not strictly comparable because of its tendency to occur in tetrahedral co-ordination. The Al/Ga ratio is often discussed in a fractionated rock series; there is usually a slight tendency for gallium to enrich relative to aluminium (see Wager and Mitchell [1] for example) and this appears to be in agreement with their respective F values. In the pair Ge^{4+}—Si^{4+}, respective F values are 86·2 and 107, and the slight trend for germanium to enrich relative to silicon in differentiated rocks (Rankama and Sahama [39] p. 730) appears to accord with respective F values. As with gallium and aluminium, the comparison is, however, not rigorous because the radius difference is large and Ge^{4+} may tend to prefer

octahedral co-ordination in silicates, whereas Si^{4+} is always tetrahedrally co-ordinated.

The behaviour of the pair Rb^+:Tl^+ in pegmatites does not accord with what would be anticipated from their respective F values of 2·84 and 4·14. Ahrens [29] has shown that the ratio Rb/Tl remains virtually unchanged throughout various replacement stages in pegmatites, whereas according to the value of F, rubidium should enrich relative to Tl in later stages of crystallization.

In the pair, Zr^{4+}:Hf^{4+}, respective F values are 43·0 and 39·0, and in a fractionated sequence, hafnium should tend to enrich relative to zirconium in crystals of late formation.

4. Melting points of olivines and of Ge *and* Ga *substituted feldspars*

The melting points of fayalite (Fe_2SiO_4) and forsterite (Mg_2SiO_4) are 1205° C and 1905° C, respectively and Goldschmidt [22] sought to explain this difference on the assumption that a shorter Mg—O distance meant greater bond strength and hence a higher melting point. Such reasoning is, however, not supported by the melting points of alkaline earth feldspars, in which melting point actually increases with increase in bond length (Table 8).

Table 8. Melting points of alkaline earth feldspars

Cation	*r* (Å)	*I* (*volts*)	*M. pt.* (°*C*)
Ba^{2+}	1·34	10·0	1720
Sr^{2+}	1·12	11·03	1660
Ca^{2+}	0·99	11·9	1553

If we assume that the metal-O bond in all silicates is slightly weakened, insofar as there must be some significant polarization-deformation of O^{2-}, it follows that substitution of one cation by another of greater polarizing power should weaken the bond to a greater extent and hence lower melting point. The respective I values for Fe^{2+} and Mg^{2+} are 16·24 and 15·03 v. Consequently the Fe—O bond should be weaker and hence the melting point of fayalite should be less than that of forsterite.

In the alkaline earth feldspars, the Ba—O bond should have the greatest proportion of ionic character, whereas that of Ca—O should be the weakest. Table 8 shows that melting point decreases with increase in I. The radii differences in the alkaline earth ions are, however, considerable and this, of course, should not be overlooked because melting point must depend to some extent on purely geometrical considerations as well.

Goldsmith [44] has synthesized and determined the properties of Ge and Ga substituted feldspars. Melting points for several albites and potash feldspars are given in Table 9.

Consider the substitution of Ge^{4+} for Si^{4+}. The respective I values are 45·7 and 45·1 v, and hence, the Ge—O bond should be slightly weaker than that of Si—O. In the pair, Al^{3+} and Ga^{3+} the I values are 28·4 and 30·7 v respectively and the Ga—O bond should be weaker than that of Al—O. Moreover, as the Al^{3+}—Ga^{3+} difference is greater than that of Si^{4+}—Ge^{4+}, substitution of Al^{3+} by Ga^{3+} should weaken the bond to a greater extent than substitution of Si^{4+} by Ge^{4+}: this accords with observation. As would, of course, be expected, the lowest melting point is found in a Ge—Ga substituted feldspar. In his discussion on the melting points of the feldspars, Goldsmith [44] mentions the possibility that melting point lowering could be caused by polarization of gallium. It is doubtful, however, whether

such highly charged small cations as Ga^{3+}, Al^{3+}, Si^{4+} and Ge^{4+} are significantly polarized and almost all deformation-polarization should take place in the electronic system associated with the large oxygen ion.

To the knowledge of the author, melting point data are not available for a Tl-feldspar, but because the I value of Tl^+ is considerably greater than that of K^+, a Tl-feldspar should have a lower melting point than potash feldspar. For the same reason, the melting point of a lead plagioclase should also be considerably lower than that of an alkaline earth plagioclase. If the I value is extremely high, as for Ag^+, Hg^{2+} and particularly Au^+, the compound may become completely unstable (see discussion No. 3).

Albite has a lower melting point than orthoclase. This may be due to the fact that the Na—O bond is weaker than that of K—O because the respective I values of Na^+ and K^+ are 5·12 and 4·34 v. However, this comparison is not rigorous because the fact that the radii of Na^+ and K^+ differ considerably is significant and the observed co-ordination of oxygen around Na^+ is somewhat distorted in feldspar, whereas such is not the case for K^+.

Table 9. Melting points of albites and potash feldspars (after Goldsmith [45])

	°C
Common albite. . . .	1118
Ge albite	1067
Ga albite	1015
Ga, Ge albite	952
Common orthoclase .	1170
Ge orthoclase	1122
Ga orthoclase	1000–1020
Ga, Ge orthoclase . .	~1000

It is of considerable interest to observe that refractive index for Ga and Ge substituted feldspar, see Goldsmith [44] increases with I; that is, refractive index tends to vary inversely with melting point. The electronic system of the anion rather than that of the cation, plays the major role in determining the refractive index properties of an ionic compound and according to Fajans and Joos [14] increased deformation of the anion should result in an elevation in the refractive index; the above observations on feldspar and olivine support this theory.

5. *Anion affinity and structure*

It was pointed out earlier that a weakness of the ionic approach was its inability to predict bond disposition in non-ionic structures. If, however, the basic assumption is correct, namely, that in the presence of a powerful force of attraction from the cation the electron distribution of the anionic partner is so deformed that varying degrees of sharing (overlap) may take place, some regularities may be expected to exist between I and structure; moreover, it should follow that the greater the ease with which a partner is deformed, the smaller the value of I required to cause a structural change.

Particular attention will be given to the mediumsized divalent cations because they provide the largest selection of graded I values. Observations will for the most part be restricted to the simplest compounds, using F^-, Cl^-, O^{2-}, and S^{2-} as partners. Of these, F^-, is by far the least deformable and is, therefore, particularly useful in many respects; S^{2-} is the most easy to polarize. The importance of making observations of this sort on the simplest compounds cannot be over-emphasized: only forces between the two partners are present and there is no other factor which may

modify the force of attraction of the cation. (See discussion below on carbonates, phosphates and sulphates.)

The structures of the oxides, sulphides and fluorides of each element are given in Table 10.

Table 10. Structures of oxides, sulphides and fluorides of divalent medium-sized cations

	Cation	*r* (Å)	*I* (*volts*)	*Oxide*	*Sulphide*	*Fluoride*
I increases →	Mg^{2+}	0·66	15·03	NaCl	NaCl	rutile
	Mn^{2+}	0·80	15·64	NaCl	NaCl, zinc blende and wurtzite	rutile
	Fe^{2+}	0·74	16·24	NaCl	NiAs	rutile
	Co^{2+}	0·72	17·4	NaCl	NiAs	rutile
	Zn^{2+}	0·74	17·95	wurtzite	zinc blende	rutile
	Ni^{2+}	0·69	18·3	NaCl*	see text	rutile
	Pt^{2+}	0·80	19·3	coplanar	coplanar	rutile
	Pd^{2+}	0·80	19·9	coplanar	coplanar	rutile? fluorite?
	Cu^{2+}	0·72	20·3	coplanar	complex (see text)	fluorite?
	Ag^{2+}	0·89	22·0	unstable	unstable	?

* Distorted below 200° C.

Symmetrical (AB) compounds

In the oxides, a major structural change appears to develop at an *I* value of ~18 v. This is not smooth, because whereas CoO and NiO both have ionic (NaCl) structures, that of ZnO is tetrahedral. It should be noted, however, that although NiO has the NaCl structure, below 200° C there is considerable distortion. Variable polarizability of the cation may be a cause for the fact that change of structure is not perfectly regular with increase in *I*. If, for example, Zn^{2+} were more easily deformed than Co^{2+} or Ni^{2+}, this property should aid in an earlier "collapse" of an otherwise ionic structure to one of lower symmetry. At *I* values greater than ~19 v a coplanar disposition of bonds obtains. Distortion and degree of complexity increase with increasing *I* (PtO→PdO→CuO—tenorite); AgO is unstable. It is not known what significance should be attached to the fact that FeO, CoO, ZnO and NiO are semiconductors.

As would be anticipated, lowering of symmetry begins at a smaller *I* value in sulphides. MnS is particularly interesting in this respect and is actually trimorphous (NaCl, zincblende and wurtzite); note also remarks about location of Mn in sulphide-silicate phase separation in discussion No.1. FeS and CoS usually have the 6:3 nickel arsenide structure, whereas that of NiS is complex and apparently sometimes shows a 5:5 co-ordination, as in millerite, and sometimes the 6:3 nickel arsenide structure. PtS and PdS structures approximate to a square coplanar arrangement; that of PdS in less symmetrical than that of PtS and shows more distortion. Interestingly enough, the structure of CuS is complex: square coplanar symmetry is replaced by triangular co-ordination of half the copper atoms, the other half having tetrahedral neighbours. It seems as if the *I* value of Cu^{2+} is too great to maintain a symmetrical square coplanar bond distribution. AgS is unstable. The mineral braggite, (Ni, Pt,

Pd)S, which shows a coplanar bond distribution is of considerable interest, because nickel, platinum and palladium appear to be capable of substitution for each other. One has the impression that because the I value of Ni^{2+} is moderately close to that of platinum and palladium it takes only a little extra effort to bend the Ni—S bond as to conform to the coplanar symmetry of the mineral as a whole. If the partner deformes more easily than S^{2-}, nickel can apparently easily form coplanar bonds, as in the cyanide complexes, $NiCN_4^{2-}$, for example.

Chalcopyrite (CuFeS) assumes the zinc blende structure which is unlike that of either of the simple sulphides FeS and CuS (see above). If I is important for determining structure, it is of some interest to note that the average I for Cu^{2+} and Fe^{2+} is 18 v which is about the same as that of Zn^{2+}. The structure of chalcopyrite could possibly be regarded, therefore, as a "compromise" structure.

If cations are bonded to anionic radicals such as SO_4^{2-}, PO_4^{3-}, CO_3^{2-}, CrO_4^{2-} and others, transition from ionic structures does not readily take place. Apparently the fact that oxygen is tightly co-ordinated in each radical prevents ions such as Ni^{2+}, Zn^{2+}, Pd^{2+} and Cu^{2+} from fully developing their ability to polarize O^{2-} (see discussion No. 3). It is for this reason that only the simplest compounds are being considered at this time in this discussion.

Asymmetrical (AB_2) compounds

Because of the characteristic ability of F^- to withstand a powerful polarizing power, stable ionic structures are found even if I is large. Rutile structures perist as far as palladium, although some distortion may be present. CuF_2 appears to have a related structure, in which, however, the Cu-F distance is anomolously long. AgF_2 is the only moderately stable simple salt of divalent silver; organic compounds, however, are known. The fact that AgF_2 is not as stable as the other difluorides and has not been prepared in the pure state seems significant: it appears that even F^- cannot satisfactorily withstand the extreme I value of 22 v. It is indeed unfortunate that no metal exists which has an I value between Cu^{2+} and Ag^{2+} because the properties of its compounds would be particularly valuable for this discussion.

When considering the chlorides, regularities are better observed if some of the larger divalent cations are included. Particular care must, however, be made to compare like sizes only, because the asymmetrical halide structures, other than the fluorides, are apparently unusually sensitive to the *size* of the cation. For example, if the chlorides of cations of identical electronic structure (Ba^{2+}, Sr^{2+}, Ca^{2+} and Mg^{2+}) are examined the following structures, Table 11, are found.

Table 11

Compound	*Radius of cation* (A)	*Structure type*
$BaCl_2$	1·35	$PbCl_2$ structure; unusual 9 co-ordination
($PbCl_2$)	(1·2)	($PbCl_2$ structure; unusual 9 co-ordination)
$SrCl_2$	1·12	8:4 fluoride structure
$CaCl_2$	0·99	deformed rutile structure
$MgCl_2$	0·66	$CdCl_2$ structure

In the pair Sr^{2+}—Hg^{2+}, radii are identical but I differs very considerably (11·03 and 18·8 v respectively). Whereas $SrCl_2$ has the typical ionic 8:4 fluorite structure, that of $HgCl_2$ is complex. Interestingly enough, Hg is octahedrally co-ordinated but 3 pairs of Cl atoms are at distinctly different distances away and it appears that the high value of I has caused this distortion. "Collapse" to lower tetrahedral co-ordination is found in HgI_2. Change of structure with increasing deformability of the partner is of considerable interest in the sequence, HgF_2. $HgCl_2$, $HgBr_2$ and HgI_2.

In the pair Ca^{2+}—Cd^{2+} in which the I difference is not as great (respective I values 11·9 and 16·9 v) $CaCl_2$ has a deformed rutile structure, whereas $CdCl_2$ has the $CdCl_2$ layer structure. The chlorides of all *medium-sized* ions from Mg^{2+}→Ni^{2+} (15 to 18·3 v; see Table 10) have the $CdCl_2$ structure; $PdCl_2$ and $CuCl_2$ form coplanar chain structures, whereas $AgCl_2$ is unstable.

Further observations on the relationship between I and structure will not be discussed here. It is no easy task to asses the physical significance of the above observations and regularities which, though not always smooth, are clearly evident. At this time only these summarized comments will be made.

(a) For ions of equal valence and like radius a lowering of symmetry is usually observable with increase in I.

(b) The value of I at which such structural changes take place depends on the deformability of the anion, and

(c) when certain regularities are viewed in detail, for example, . . . NiO—PtO—PdO—CuO—AgO, and . . . NiS—PtS—PdS—CuS—AgS, changes occur which may be of considerable significance for understanding the nature of bonds.

6. *The use of ionic radii in sulphide minerals*

Although the bonds in sulphide minerals have a high degree of covalent character. the interpretation of the geochemical classification of elements in discussion No. 1 has been made possible through the ionic approach, and this in itself justifies, to some extent at least, the use of ionic radii in sulphide minerals. However, as these structures are not determined by a packing of ionic spheres according to the usual radius ratio rules [exceptions, PbS (NaCl structure) and MnS, which can assume an NaCl structure as well as non-ionic structures], no large-scale substitution does take place. During the precipitation of a sulphide mineral crystal, ions of equivalent size and valence will presumably be assembled together in the liquid in the process of competing for a given site, and although the bond disposition to sulphur of each individual element may differ in the product, it is likely to be captured to some extent in the host structure. This is visualized more easily if the assumption is made that bonds are bent to a certain disposition rather than that they assume a fixed disposition by hybridization of bond orbitals—see discussion No. 5. It follows from this reasoning that the smaller the difference in polarizing power the easier it is for bonds of a minor constituent to be accepted into the covalent structure of the host. In general this seems to be the case.

Pyrrhotite and pyrite are two of the commonest sulphide minerals in rocks (Newhouse [45]) and those divalent elements which have ions of a medium size (0·6–0·8 Å) are the commonest minor constituents in these minerals. Moreover, high-temperature pyrrhotite and also early pyrite, are often characteristically en-

riched with elements whose ions have F values $> Fe^{2+}$, namely, Co^{2+}, Zn^{2+}, Ni^{2+}, Pt^{2+}, Pd^{2+} and Cu^{2+}. See, for example, analyses of I. and W. NODDACK [24] and discussion by RANKAMA and SAHAMA ([39], p. 98). The enrichment of nickel in early pyrrhotite—pentlandite is common (compare with silicates; discussion No. 3), and in this respect the association of palladium and platinum with nickel in such minerals is particularly interesting and may be anticipated from their I and F values. (The Ni, Pt, Pd substitution in braggite is referred to in discussion No. 5.) Although concentrations of a few percent copper may be found in early high-temperature FeS, as at Sudbury, Canada, for example, really high concentrations cannot be accepted by the FeS structure because of a large I difference. In the presence of high concentrations of both copper and iron, calcopyrite is apparently formed; see discussion No. 5.

Traces of many chalcophile elements are found in sphalerite. The greatest concentration is frequently that of iron and several percent may be present. Here again moderately large-scale substitution is apparently possible because the ionic radii of iron and zinc are similar and because the difference in I is not excessive.

Some of the most characteristic minor constituents of galena are silver and bismuth. Ionic radii are $Pb^{2+} = 1{\cdot}20$, $Ag^{+} = 1{\cdot}26$, and $Bi^{3+} = 0{\cdot}96$. These are typically large cations and concentrations of elements which have cations of smaller radii, for example Cu^{2+}, Fe^{2+}, As^{3+} and others, are usually much lower than those of the large-radii elements. Mercury is not enriched in galena, despite its favorable radius (1·12 Å) and one possible cause is that its I value is extreme for such a large ion; 18·8 v as compared with 15·04 v for Pb^{2+}.

Without proceeding any further, one may conclude that ionic radii may be used in a rather restricted way in sulphide minerals. The fact, however, that the distribution of elements in sulphides cannot be handled nearly as satisfactorily as in silicates, is not only due to the covalent nature of the bond, but also to the characteristic ability of a sulphide precipitate to co-precipitate and occlude a large variety of elements. Analytical chemists are well aware of this annoying tendency.

An example in sulphides of ionic substitution in the usual sense, is that of Mn^{2+} in CaS (oldhamite, a mineral which is confined to meteorites (see GOLDSCHMIDT [46]). Because of the moderately small I value of Mn^{2+}, MnS is just able to retain an NaCl structure and considerable substitution of Mn^{2+} ($r = 0{\cdot}80$ Å) for Ca^{2+} ($r = 0{\cdot}99$ Å) takes place despite a moderately large radius difference.

7. Formation of complexes in solution

The ability of highly charged ions such as S^{6+}, N^{5+}, C^{4+}, Cr^{6+}, Mn^{7+} (but note, not Br^{7+}) to bind oxygen into complexes (SO_4^{2-}, NO_3^{-}, CO_3^{2-}, CrO_4^{2-}, MnO_4^{-}) which are not dissociated by a strong dielectric such as water, is reasonably well understood if the ionic approach to the formation of bonds is employed. In this respect the ionic potential has been used (GOLDSCHMIDT [22]) to indicate which elements are capable of being transported as complexes in water during the sedimentary cycle. These highly-charged ions have, of course, extremely high I values and anion affinity will be used in this discussion because it takes into consideration variable screening of the nucleus and can consequently be used for interpreting the characteristic ability of a monovalent element such as aurous gold to form stable complexes.

Before proceeding to discuss complex formation in geological materials, some well-known examples of stable complexes will be discussed in order to ascertain to what extent complex formation is supported by the approach used here. In general, the underlying philosophy is that in the presence of a large anion affinity the anionic partner may become bound to the cation in the form of a complex (see Fajans [16]). The properties of the anionic partner are particularly important in determining whether complex formation is to occur under certain conditions or not. For example, O^{2-} is readily bound into stable complexes with the above small highly-charged cations, whereas S^{2-} is not; on the other hand, the large and easily deformed S^{2-} is readily bound to a large univalent cation (Au^{+}) to give AuS^{-} (see below). Easily deformed CN^{-} requires about the lowest I value of all for complex formation, yet is apparently not stable in the presence of small highly-charged cations (C^{4+}, S^{6+}, etc.); OH^{-} responds to varying I values in a totally different way.

In discussions Nos. 3 and 4, it was pointed out that for a given partner, an increase in I weakens the bond; alternately, for constant I, the bond weakens with increase in the polarizability of the partner. However, with extremely high I values, complex formation develops. Thus in the sequence $AgF \rightarrow AgCl \rightarrow AgI \ldots Ag(CN)_2^-$ the bond weakens in passing from $F \rightarrow I$, but the Ag—CN bond in the complex, $Ag(CN)_2^-$, is stable.

Consider the medium-sized divalent cations (Mg^{2+}, Cu^{2+} of Table 2). Those with the greatest anion affinity are able to form complexes with a variety of simple anions and radicals, and much of their chemistry is that of complexes; $PtCl_4^{2-}$ is, for example, one of the best known stable complexes. Of the large divalent cations ($Ba^{2+} \rightarrow Hg^{2+}$), Hg^{2+} ($I = 18{\cdot}8$ v) in particular has a marked ability to hold a wide variety of radicals in complexes; Cd^{2+} ($I = 16{\cdot}9$ v) shows this tendency but to a much lesser extent. Related to the ability to form complexes, is the dissociation of salts: those of mercury usually ionize poorly and, as would be anticipated, the order of decrease of dissociation is fluoride, chloride, bromide and cyanide. Of the univalent elements, gold shows by far the greatest tendency to form complexes; not only is the I value so high (for a univalent element) that gold is particularly loath to react, but when it does it invariably binds the anionic partner into a complex. Copper and silver also show a well-developed tendency for complex formation, but not nerarly so great as that of gold. The heptavalent cations, Mn^{7+}, Cl^{7+}, and Br^{7+} (respective I values, $\sim$122, 114 and 103·5 v) are of some interest. No perbromates are known but perchlorates and permanganates are well known and moreover the stability of MnO_4^- is considerably greater than that of ClO_4^-; stability appears to vary with the value of I. Wells [6] notes that of the trivalent elements iron, chromium and cobalt by far the greatest tendency to form complexes is shown by cobalt, followed by chromium; iron shows a much weaker tendency: this is in the order of their I values. Interestingly enough, the properties of many quadrivalent ions, including that of their ability to form complex compounds, are in general similar. This is to be expected from the fact that with few exceptions the fourth ionization potentials of quadrivalent cations of approximately the same size are similar.

The discussion so far has been general and it may be concluded from the various regularities noted above that the value of the anion affinity is apperently important in determining the ability of elements to form complexes.

A high dilution tends to cause dissociation of a complex and in environments as are found in the sedimentary cycle only the oxygen complexes of the small highly-charged cations would be stable; the particular state of oxidation won't be discussed here. In the oceans, however, complex formation with Cl^- by cations of large I value is possible because of a high concentration of Cl^-; some copper and palladium could, for example, be held as $CuCl_4^{2-}$ and $PdCl_4^{2-}$.

Krauskopf [47] has shown that in naturally occurring alkaline solutions, gold is significantly soluble in the presence of sulphides and is carried as a complex anion AuS^-. Krauskopf points out that the complex AuS^- must be exceptionally stable because metallic gold is soluble in HS^- solution at ordinary temperatures. It is not known to what extent, if any, CuS^- and AgS^- complexes may be found under like circumstances; the I values for Cu^+ and Ag^+ are large but considerably smaller than that of Au^+. Standard electrode potentials (Krauskopf [47]) show that neither Au^+, nor the higher valence state Au^{3+} can exist in solution as simple ions in geological environments. Au^+ is not apparently able to bind O^{2-} into AuO^- under these conditions and unless an appropriate partner is available for complex formation (S^{2-} and Cl^-), gold will precipitate as the metal. Gold is generally regarded as a geochemically mobile element and there is little doubt that much of this is due to its unique ability in being able to form stable complexes in an aqueous solution.

Aurous gold shows slight amphoteric tendencies which are presumably due to its high I value, but it is not known whether this property is geochemically significant.

The geochemistry of gold is unique and is one of extremes. Because of its extremely high I value it has a marked tendency to occur native and if it does react, complexes invariably form and simple compounds are extremely rare. Such geochemical behaviour is, of course, a direct consequence of the effect of entry of $4f$ electrons (lanthanide contraction).

8. Ionization potentials and stable valence states

The maximum stable valence state of an element is usually given by its location in the periodic table. There are, of course, exceptions; for example, the Group 1b elements may show a valence greater than one. In aqueous solution oxidation-reduction potentials may be used indicate the state of ionization (oxidation). Ionization potentials may, however, be used in a rather general way to indicate all the possible valence states which an element may assume. They have the advantage of indicating by measurement why such transitory states as Fe^+, Mg^+, Si^{3+}, and others are never found in chemical combination; in addition they provide measured indications of the extent to which ionization may proceed in chemical combination. Although ionization potentials are useful in their general way, it must be borne in mind that they are properties of free ions and cannot replace, therefore, oxidation potentials when exact information is required about the state of oxidation of an element in an aqueous solution. For a discussion of the use of oxidation potentials during the sedimentary cycle, see Scerbina [48] and Mason [25].

Table 12(a) gives the first five ionization potentials for the Group 4 elements and Table 12(b) gives ionization potential differences (Δ): subscripts will be used to indicate the two particular states in question; for example, $\Delta 1, 2$ indicates the difference between the first and second ionization potentials.

Table 12

(a) *Ionization potentials of Group IV elements*

	I_1	I_2	I_3	I_4	I_5
Si	8·15	16·34	33·49	45·13	166·5
Ge	8·13	15·93	34·22	45·70	93·43
Ti	6·84	13·60	27·50	43·24	99·84
Sn	7·33	14·60	30·65	40·74	81·13
Zr	6·95	14·03	24·10	33·97	?
Pb	7·40	15·04	32·1	38·97	69·7
Ce	6·6	calc. 13·2	19·7	36·7	?

(b) *Ionization potential differences* (Δ)

	$\Delta_{0,1}$	$\Delta_{1,2}$	$\Delta_{2,3}$	$\Delta_{3,4}$	$\Delta_{4,5}$
Si	8·15	8·2	17·15	11·64	121·4
Ge	8·13	7·8	17·3	11·50	47·73
Ti	6·84	6·8	~13·9	~15·74	56·60
Sn	7·33	7·31	16·0	10·10	40·40
Zr	6·95	7·18	10·10	9·9	>20·0 ?
Pb	7·40	7·64	17·1	6·9	30·7
Ce	~6·6	calc. 6·6	calc. 6·5	17·0	>20·0 ?

For each element the 5th ionization potential is much greater than the 4th and because $\Delta_{4,5}$ is so large, no valence states > 4 are ever attained by these elements. It seems that if Δ is larger than ~20–30 v, ionization cannot proceed further in chemical combination. This conclusion is based in part on the I values given in this discussion and on some unpublished data. On the other hand, if Δ is ~8–10 v or less, the state of higher ionization is never stable and ionization immediately takes place to higher states until larger Δ values are reached. These values are merely magnitudes and when critical comparisons are made it will become apparent that some allowance must be made for size and weight; for example, silicon should not be compared with lead, but rather with germanium, while zirconium is best compared with lead. One general observation on the Group IV elements is that the second ionization potential is about double that of the first; the other periodic groups of elements do not show this.

Consider the pair Si:Ge. The first 4 ionization potentials of silicon are very similar to those of germanium. (The possible significant difference in their 4th ionization potentials is referred to in discussion No. 4.) Because $\Delta_{1,2}$ is small, there is no stable univalent state, but because $\Delta_{2,3}$ is moderately large, divalent states are possible and are known. Germanium has the greater value $\Delta_{2,3}$ and this apparently the cause for the fact that divalent germanium shows considerable stability; in fact, although no divalent silicon compounds are found in a geological environment, divalent germanium may apparently be found in some sulphide minerals. For both elements $\Delta_{3,4}$ is small with the result that ionization is not held up at the trivalent state and always proceeds on to the quadrivalent state where because $\Delta_{4,5}$ is large no higher degree of ionization is ever found in chemical combination.

In the pair Ti:Sn, the latter shows a similar I value pattern to that of germanium and silicon, whereas that of titanium is distinctly different. Divalent tin compounds

are known in geological environment in sulphide minerals, but the commonest valence is 4. Titanium may show a feeble tendency to form divalent compounds because $\Delta_{2,3}$ is ~13·9 v, but the trivalent state is much commoner because $\Delta_{3,4}$ is moderately large and trivalent titanium may be found in a mildly reducing geological environment, as in igneous rocks of early formation in a differentiated suite. In most geological environments, however, titanium is quadrivalent because the value of ~15·74 v for $\Delta_{3,4}$ is not very large, whereas that of $\Delta_{4,5}$ is extreme (56·6 v).

The pair Zr:Pb make an interesting comparison. Δ values for zirconium are all low (<10·1 v) and consequently no low valence states of zirconium are ever found in a geological environment because "oxidation" up to the quadrivalent state is always immediate. On the contrary, ionization in lead is held up at the divalent state because $\Delta_{2,3}$ is large for a heavy element and in most geological environments, lead is always divalent. $\Delta_{3,4}$ is small, whereas $\Delta_{4,5}$ is large and consequently if lead is exposed to a powerful oxidation environment, ionization will continue to the 4th state. Conditions of powerful oxidation may prevail in the sedimentary cycle and consequently quadrivalent lead, as in plattnerite, may be found. The second ionization potential of cerium is not known, but it must be low and about equal to that of the first (see remarks above in this respect). Consequently because $\Delta_{1,2}$ and $\Delta_{2,3}$ are small, whereas $\Delta_{3,4}$ is moderately large, trivalent cerium is a stable state and as a result cerium is trivalent in many minerals; however, $\Delta_{3,4}$ is not exorbitant and quadrivalent cerium compounds are common.

Table 13 gives I and Δ values for Group I elements.

Table 13. Ionization potentials and ionization potential differences for Group I elements

	I_1	I_2	I_3	$\Delta_{0,1}$	$\Delta_{1,2}$	$\Delta_{2,3}$
Na	5·15	47·30		5·15	42·16	
K	4·34	31·80		4·34	27·46	
Rb	4·18	27·5		4·18	23·32	
Cs	3·89	32·49		3·89	28·60	
Cu	7·72	20·28	37·10	7·72	12·56	16·82
Ag	7·57	22·00	36·0	7·57	14·43	14·0
Au	9·22	20·1	~31·0	9·22	10·78	~10

For the 8-electron elements $\Delta_{1,2}$ is always > 23 v and as a result they are characteristically univalent. For the 18-electron elements $\Delta_{1,2}$ increases in the order Au, Cu and Ag. Gold forms monovalent compounds but because $\Delta_{1,2}$ and $\Delta_{2,3}$ are small, ionization to a higher state is immediate in an oxidizing environment and gold is also trivalent. In a geological environment both mono- and divalent copper compounds may be found, but because $\Delta_{1,2}$ is moderately small the divalent state is by far the commonest. By comparison, however, $\Delta_{1,2}$ is almost 2 v greater in silver, and as a result univalent silver is the only stable state in geological environments. Under conditions of extreme oxidation and in complex formation, divalent silver may be found.

Table 14 shows I and Δ values for some Group V elements.

$\Delta_{1,2}$ values are small for each element and as a result monovalent compounds are unstable. Vanadium shows the largest value of $\Delta_{2,3}$ and this is the only element in this group which shows a tendency to be divalent, although such a valence is

Table 14

(a) *Ionization potentials of Group V elements*

	I_1	I_2	I_3	I_4	I_5	I_6
P	10·98	19·65	30·16	51·37	65·01	large
As	10·5	20·2	27·3	50·12	52·6	large
V	6·74	14·2	~26·5	~48·5	~64	large
Sb	8·64	~18·6	24·83	44·10	55·7	large

(b) *Ionization potential differences* (Δ)

	$\Delta_{0,1}$	$\Delta_{1,2}$	$\Delta_{2,3}$	$\Delta_{3,4}$	$\Delta_{4,5}$	$\Delta_{5,6}$
P	10·98	8·67	10·51	20·20	13·64	large
As	10·5	9·8	7·1	22·82	12·48	large
V	6·74	7·46	~12·3	~22·0	~15·5	large
Sb	8·64	9·96	6·23	21·27	11·6	large

not well developed because further oxidation usually takes place. It is highly unlikely that divalent vanadium would ever be found in a geological environment. For each element $\Delta_{3,4}$ is large (~20–23 v) and as a consequence each element shows a marked tendency to be trivalent. In a geological environment, trivalent As, Sb and V are common. By far the largest $\Delta_{4,5}$ value is that shown by vanadium and it is only this element which shows a definite tendency to form stable quadrivalent compounds, and it is probable that vanadium is sometimes quadrivalent in nature, but because $\Delta_{4,5}$ is not exorbitant, oxidation to the quinquevalent state is quite common. This state is stable for each element in the group because $\Delta_{5,6}$ is apparently always excessively large.

In the trio, Fe, Co and Ni, $\Delta_{1,2}$ is small ($<11{\cdot}0$ v) whereas $\Delta_{2,3}$ is moderate; 14·4, ~16·6 and ~17·8 v, respectively. As a result no univalent compounds exist, whereas divalent compounds are common. Ease of oxidation of divalent Fe, Co and Ni in an aqueous solution (as determined by oxidation potentials) follows the same order as that of ionization of the free cations. Both di- and trivalent iron are found in igneous rocks, whereas only divalent cobalt and nickel occur. During the sedimentary cycle, oxidation of cobalt to the trivalent state may take place, but the oxidation environment is never sufficiently intense to produce trivalent nickel. Fluorine, the element with the greatest electron affinity, is able to oxidize nickel to the trivalent state as in NiF_3.

References

[1] Wager, L. R. and Mitchell, R. L.; The distribution of trace elements during strong fractionation of basic magma—a further study of the Skaergaard intrusion, East Greenland. Geochim. et Cosmochim. Acta 1951 **1** 129. [2] Lewis, G. N.; The atom and the molecule. J. Amer. Chem. Soc. 1916 **38** 762. [3] Pauling, L.; The nature of the chemical bond. 2d. Ed. Cornell University Press 1945. [4] Slater, J. C.; Directed valence in polyatomic molecules. Phys. Rev. 1931 **37** 481. [5] Pauling, L.; The nature of the chemical bond. Application of results obtained from the quantum mechanics and from a theory of paramagnetic susceptibility to the structure of molecules. J. Amer. Chem. Soc. 1931 **53** 1367. [6] Wells, A. F.; Structural inorganic chemistry. 2d. Ed. Clarendon Press, Oxford 1950. [7] Wells, A. F.; Bond lengths in some inorganic molecules and complex ions. J. Chem. Soc. for

1949, p. 55. [8] Stevenson, D. P. and Schomaker, V.: Some revisions of the covalent radii and the additivity rule for the lengths of partially ionic single covalent bonds. J. Amer. Chem. Soc. 1941 **63** 37. [9] Mulliken, R. S.; A new electroaffinity scale; together with data on valence states and on valence ionization potentials and electron affinities. J. Chem. Phys. 1934 **2** 782. [10] Mulliken, R. S.; Electronic structures of molecules. I. Electroaffinity, molecular orbitals and dipole moments. J. Chem. Phys. 1935 **3** 573. [11] Ramberg, H.: Verbal communication, 1951. [12] Fyfe, W. S.; Isomorphism and bond type. Amer. Mineral 1951 **36** 538. [13] Gruner, J. W.; An attempt to arrange silicates in the order of reaction energies at relatively low temperatures. Amer. Mineral 1950 **35** 137. [14] Fajans, K. and Joos, G.; Molrefraktion von Ionen und Molekülen im Lichte der Atomstruktur. Z. Phys. 1924 **23** 1. [15] Fajans, K.; Die Eigenschaften salyartiger Verbindungen und Atombau. II. Z. Krist. 1928 **66** 321. [16] Fajans, K.; The molar dispersion and refraction of free and bonded ions. J. Amer. Chem. Soc. 1942 **64** 3023. [17] Goldschmidt, V. M.; Geochemische Verteilungsgesetze der Elemente. VII and VIII. Skrift. Norske. Vid.-Akad., Oslo, Mat.-Nat. Kl., 1926, Nos. 2 and 8. [18] Förland, T. and Weyl, W. A.; Distribution of heavy metal ions in silicates containing several anions of different size. J. Amer. Ceram. Soc. 1949 **32** 267. [19] Cartledge, G. H.; Studies on the periodic system—I, II, III. J. Amer. Chem. Soc. 1928 **50** 2855; 1930 **52** 3076. [20] Dietzel, A.: Cation field intensities and their relations to devitrification phenomena, to formation of compounds and to melting points of silicates. Z. Elektrochem. 1942 **48** 9. [21] Glasstone, S.; Textbook of physical chemistry. 2d. Ed. Van Nostrand, New York 1946. [22] Goldschmidt, V. M.; The principles of distribution of chemical elements in minerals and rocks. J. Chem. Soc. for 1937, p. 655. [23] Neumann, H.: Notes on the mineralogy and geochemistry of zinc. Min. Mag. 1949 **28** 575. [24] Noddack, I. and Noddack, W.; Die Geochemie des Rheniums. Z. phys. Chem. A 1931 **154** 207. [25] Mason, B.; Oxidation and reduction in geochemistry. J. Geol. 1949 **57** 62. [26] Ahrens, L. H., Pinson, W. H. and Kearns, M. M.; Association of potassium and rubidium and their abundance in common igneous rocks and meteorites. Geochim. Cosmochim. Acta 1952 **2** 229. [27] Canney, F. C.; Association of potassium, rubidium, cesium and thallium in sediments. 1952. Ph.D. thesis, Dept. of Geology, M.I.T. [28] Eugster, H. P.; Unpublished data. [29] Ahrens, L. H.; The unique association of thallium and rubidium in minerals. J. Geol. 1948 **56** 578. [30] Goldschmidt, V. M. and Peters, Cl.; Zur Geochemie des Galliums. Nachr. Wiss. Göttingen, Math.-Phys. Kl., 1931 **4** 165. [31] Nockolds, S. R. and Mitchell, R. L.; The geochemistry of some Caledonian plutonic rocks: a study in the relationship between the major and trace elements of igneous rocks and their minerals. Trans. Roy. Soc. Edinburgh 1948 **61** 533. [32] Ahrens, L. H. and co-workers; Unpublished data, Dept. of Geology, M.I.T. [33] Bell, C. K.; Unpublished data. [34] Rankama, K.; A note on the geochemistry of thallium. J. Geol. 1949 **57** 608. [35] Shaw, D. M.; The geochemistry of indium. In press. [36] Rankama, K.; On the geochemistry of tantalum. Bull. Comm. géol. Finlande 1944 **133**. [37] Rankama, K.; On the geochemistry of niobium. Ann. Acad. Sci. Fennicae A 1948 **3**. [38] Wickman, F. E.; Some aspects of the geochemistry of igneous rocks and of differentiation by crystallization. Geol. Fören. Stockholm Förh. 1943 **65** 371. [39] Rankama, K. and Sahama Th. G.; Geochemistry. University of Chicago Press, 1950. [40] Bray, J. M.; Spectroscopic distribution of minor elements in igneous rocks from Jamestown, Colorado. Bull. Geol. Soc. Amer. 1942 **53** 765. [41] Goldschmidt, V. M.; Crystal chemistry and geochemistry. Chem. Prod. 1944 **7** 1. [42] Walker, F. and Ahrens, L. H.; Unpublished data. [43] Sandell, E. B. and Goldich, S. S.; The rarer metallic constituents of some American igneous rocks. J. Geol. 1943 **51** 99. [44] Goldsmith, J.; Gallium and germanium substitutions in synthetic feldspars. J. Geol. 1950 **58** 518. [45] Newhouse, W. H.; Opaque oxides and sulphides in common igneous rocks. Bull. Geol. Soc. Amer. 1936 **47** 1. [46] Goldschmidt, V. M.; Geochemische Verteilungsgesetze der Elemente. IX. Die Mengenverhältnisse der Elemente und der Atom-Arten. Skrift. Norske Vid. Akad., Oslo. Mat.-Nat. Kl. 1938 **4** 1. [47] Krauskopf, K. B.; The solubility of gold. Econ. Geol. 1951 **46** 858. [48] Scerbina, V. V.; Oxidation-reduction potentials as applied to the study of the paragenesis of minerals. Acad. Sci. U.R.S.S. Bull. 1939 **22** 503.

Geochimica et Cosmochimica Acta, 1953, Vol. 3, pp. 30 to 33. Pergamon Press Ltd., London

The hafnium to zirconium abundance ratio and specific radioactivity of some ores

R. A. Cooley, A. V. Martin, C. Feldman and J. Gillespie

(Received 3 December 1951)

ABSTRACT

The hafnium to zirconium abundance ratio and the specific radioactivity of some ores from different continents were measured spectroscopically and by Geiger counter respectively. Hevesys postulation of a relationship between the radioactivity and hafnium content of zircons and the possibility of the abundance ratio serving as a geological indicator are discussed.

Introduction

Values of the hafnium to zirconium abundance ratios in ores from various sources are of interest because these ratios have been rather trouble-some to obtain with a high degree of certainty prior to the development of the spectroscopic method [1]. The abundance ratios coupled with radioactivity measurements permit the testing of the generalization [2], [3] first proposed by Hevesy, that "the radioactivity of zircons accordingly shows a rough paralellism with their hafnium content."

The abundance ratio of hafnium to zirconium in ores from places in various continents [4]–[11] has been reported to vary from 0·00279 to 0·323, *i.e.*, by a factor of about 120.

In addition to academic questions concerning the significance of the abundance ratio of hafnium to zirconium, a practical concern in the deposits of these elements throughout the world is developing. Zirconium free of hafnium might serve as a structural material [12] in nuclear reactors. Hafnium-containing metals are of possible use since a mixture of hafnium and zirconium carbide [13] is one of the highest melting solids.

The abundance ratio of hafnium to zirconium in a few ores * from North America, South America, Australia and India were determined spectroscopically and the specific radioactivity of some of these was measured.

Experimental Work

A. Determination of the specific radioactivity of ores

The relative specific radioactivities of the ores were determined by placing 0·500 g of the finely divided ore sample in an aluminium planchet one inch in diameter. The planchet was vibrated until the thickness of the sample appeared uniform. The filled planchet was then placed in a holder which was inserted into a lead shield 1 cm from a 10 mg/cm^2 aluminium thyrode counter tube (type 1B 85 *Victoreen Instrument Co.*). The counter tube was connected to a *Nuclear Corp.* Scaling Unit type 161. The period of counting varied for each sample and was made long enough so that

* The first six ores listed in Table 1 were kindly supplied by Prof. A. W. Schlecten, Chairman of the Department of Metallurgy, University of Missouri School of Mines and Metallurgy.

the probable maximum error was less than 2% for the more active samples and not more than 10% for the least active. The results of these measurements are shown in Table 1.

Table 1. Specific radioactivity and Hf *to* Zr *abundance ratio in some ores*

No.	*Sample*	*Source*	Hf/Zr *Abundance ratio*	*Specific radioactivity in counts/min*
1	Zircon	Florida	0·027	10±1·0
2	Zircon	Coos Bay, Oregon	0·023	16·4±1·0
2 dup.	Zircon	Coos Bay, Oregon	0·023	
3	Zircon	India	0·020	14·2±1·0
3 dup.	Zircon	India	0·019	
4	Zircon	Australia	0·019	12·4±1·0
4 dup.	Zircon	Australia	0·018	
5	Baddelyite	Poços de Caldas, So. Am.	0·013	235·8±3·7
5 dup.	Baddelyite	Poços de Caldas, So. Am.	0·013	162·0±2·9
6	Zirkite	Brazil	0·012	162·0±2·9
7	ZrO_2 reagent	Old Lab. bottle	0·010	
8	Zircon	Brazil	0·0078	
9	Zircon	Brazil	0·015	
10	Baddelyite	Colorado	0·068	
11	Zircon	Brazil	0·010	
12	Zircon	North Carolina	0·016	
13	Zircon	Berks Co., Pa.	0·026	
14	Zircon	Queensland, Australia	0·015	

B. Separation of mixed zirconium and hafnium from ores

To determine the abundance ratio of hafnium to zirconium a spectrographic analysis was made on a sample of zirconium and hafnium separated from the ore sample. This separation can be accomplished in a variety of ways [14] depending on the composition of the ores.

After a little exploratory work we adopted the following procedure as the most satisfactory:

A one gram sample of ore was submitted to a sodium peroxide fusion in a nickel crucible protected with sodium carbonate. The melt was placed in water and the solution was made 0·3 N in HCl. H_2S was then bubbled into the solution to precipitate group II ions. Tartaric acid was added to the filtrate to complex the Zr and Hf ions. NH_4OH was then added and H_2S was introduced to precipitate group III ions. The filtrate was boiled to remove H_2S and concentrated H_2SO_4 was added until the resulting solution was 10% H_2SO_4 by volume. The solution was cooled to 10° and 6 gm of cupferron (Nitrosophenylhydroxylamine) was added to give a white curdy precipitate which was washed with 1 to 10 cold HCl. The cupferron precipitate was dried and heated until only Zr–Hf oxide remained. The Zr–Hf oxide was fused with 10 gm of potassium pyrosulphate. The melt was dissolved in hot 1% H_2SO_4. NaOH was added until precipitation started, then NH_4OH was used to complete the precipitation. The precipitate was dissolved in a minimum of concentrated H_2SO_4 and diluted with 10% H_2SO_4 until the metal ion concentration was approximately 1%. It is believed that the cupferron precipitated essentially all Hf and Zr and did not cause any separation of the two.

C. Spectrographic determination

The spectrographic method used was that described by Feldman [1]. The above described solution was introduced into a porous carbon cup electrode and the resulting relative intensity of the lines Hf II 2641·406, Hf II 2820·224, Zr 2761·911 and Zr II 2583·405 as determined by a *A.R.L.-Dietert* Spectrograph and *L. and N.* Microphotometer indicated the Hf to Zr ratio. The values of the abundance ratio are believed accurate to $\pm 5\%$.

Discussion

The radioactivity of zirconium (hafnium) minerals has been attributed [15], [16] to the presence of thorium and uranium which are reported [17] to be ismorphous with hafnium. Some zircons are reported [18] to swell on grinding and liberate appreciable quantities of helium. Altered zircon, which is one of the richest sources of hafnium, has been thought by some authors [19], [20] to be metamict, *i.e.* partially amorphous, due to crystal breakdown caused by alpha particles from some included radioactive element. However Böhm and Ganter [16] found no relation between metamict nature and hafnium content of minerals. Morgan [22] in a study of the relation between chemical composition and refractive index of zircons of several types found no relation between specific radioactivity and hafnium content. The limited number of determinations in Table 1 do not indicate that the specific radioactivity of an ore in general is an indication of its hafnium content although limiting consideration to zircons alone gives a 75% correlation. The radioactivity associated with zircons and other hafniferous minerals may have a significance which could be unraveled by a quantitative study of thorium, uranium and hafnium in minerals. but at present it is an uncertain although convenient prospector's indicator.

There are very few direct check analyses on the abundance ratio. Prandtl [11] and coworkers obtained a value of 0·012 for an ore sample from Sierra de Caldas, Brazil. Franco and Loewenstein [10] state that their analyses of ores in this region have a value from 0·01 to 0·03.

Ores with high values of the hafnium to zirconium ratio are difficult to locate* [5]. The results in Table 1 do not show a very large range in abundance ratios, 0·0078 to 0·068, considering the distance between the sources.

One might question (1) whether any appreciable separation of zirconium and hafnium has occurred due to geological processes and (2) the rather detailed explanation for the present distribution of zirconium and hafnium advanced by Hevesy [15]. If the ratio of hafnium to zirconium is a characteristic of different parts of the earth, then the ratio might be used as an indicator [22] of continent history. Some separation may have occurred due to geological processes** but it is not necessary to assume as Hevesy suggests [15] that the initial ratio of hafnium to zirconium was a constant of about 0·017 in the gaseons-liquid earth and that natural chemical separation since then accounts for the present distribution. An alternate possibility is the following. Hafnium and zirconium (or one of the two) may

* Prof. E. M. Larsen kindly permitted us to read his notes on an interesting inquiry into the availability of hafniferous minerals in ten states, Brazil, Canada, Madagascar and Norway.

** The reported [2] difference in the ratio in the nucleus and in the shell of lavas is a very interesting observation that needs explanation.

have been formed from some unstable elements. The abundance ratio of these unstable elements may or may not have been a constant when the earth was in a gaseo-liquid state. Geological processes may have separated these unstable elements, provided their lifetimes are long enough, much more readily than they could have separated zirconium and hafnium. Deposits of the unstable elements in various ratios could thus give rise to deposits with different hafnium to zirconium ratios without requiring chemical processes in the earth to separate zirconium and hafnium which have only recently been separated in the laboratory with reasonable ease [23], [24], [25].

References

[1] Feldman, C.; Anal. Chem. 1949 **21** 1041; 1949 **21** 1211. [2] Hevesy, G. v.; Chem. Rev. 1925 **2** 31. [3] Piutti, A.; Rend. accad. sci. Napoli 1925 **31** 72. [4] Hevesy, G. v. and Jantzen, V. T.; J. Chem. Soc. 1923 **123** 3218. [5] Hevesy, G. v. and Jantzen, V. T.; Z. anorg. allgem. Chem. 1924 **136** 387. [6] Lee, O. I.; Chem. Rev. 1928 **5** 17. [7] Hevesy, G. v. and Wurstlin, K.; Z. Physik Chem. 1928 **139 A** 605. [8] Troger, E.; Chem. Erde 1935 **9** 286. [9] Kostyleya, E. E.; Khim. Referat. Zhur. 1941 **4** No. 6, 30. [10] Franco, R. R. and Loewenstein, W.; Am. Mineralogist 1948 **33** 149. [11] Prandtl, W., Mayer, G. and Buttner, L.; Z. anorg. allgem. Chem. 1937 **230** 419. [12] Chem. Eng. News 1949 **27** 223. [13] Hevesy, G. v.; Chemical Analysis by X-rays and Its Applications, p. 197. McGraw-Hill, 1932. [14] Scott's Standard Methods of Analysis, D. Van Nostrand Co., New York 1939. [15] Hevesy, G. v.; J. Chem. Soc. 1931 **9**. [16] Chudoba and Stackelberg, M. v.; Z. Krist. 1937 **95** 230. [17] Fernandes, L.; Atti accad. Lincei 1925 **2** (6) 182. [18] Liddell, D. M.; Eng. Mining J. 1917 **104** 153. [19] Chudoba and Stackelberg, M. v.; Z. Krist. 1937 **97** 252. [20] Leitz; Z. Krist. 1937 **98** 201. [21] Morgan, J. H.; Ph. D. *Thesis*, University of Wisconsin, 1940. [22] Engel, A. E. J.; Engineering and Science 1951 **14** 5. [23] Street, K. and Seaborg, G. T.; J. A. C. S. 1948 **70** 4268. [24] Kraus, K. A. and Moore, G. E.; J. A. C. S 1949 **71** 3262. [25] Hansen, R. H. and Gunnar, K.; J. Amer. Chem. Soc. 1949 **71** 4158.

Geochimica et Cosmochimica Acta, 1953, Vol. 3, pp. 34 to 46. Pergamon Press Ltd., London

Minor element content of Ontario diabase*

H. W. Fairbairn, L. H. Ahrens and Lorraine G. Gorfinkle

Department of Geology and Geophysics, Massachusetts Institute of Technology

ABSTRACT

The following elements (Ni, Co, V, Cr, Cu, Ag, Pb, Sc, Zr, La, Ga, Sr, Ba, Li, Rb and K) have been determined quantitatively in 59 specimens of Ontario diabase from representative areas and in 3 specimens of Duluth gabbro, using spectrochemical.procedures. The data are presented in the form of frequency distribution diagrams. Average abundances have been computed and are compared with other values for diabase and similar compositional types. Of the elements studied gallium shows by far the greatest uniformity of concentration in diabase, in contrast to chromium which shows the largest scatter. The largest discrepancy between a published abundance value and one given here is that of scandium, and our results indicate that earlier values are usually too low by a factor of about 3.

In order to reduce systematic analytical error to a minimum, all results given here have been calibrated in terms of Standard diabase W-1 (see U.S.G.S. Bulletin No. 980).

Introduction

As a part of a general study at M.I.T. of occurrence and distribution of minor elements in common rocks and minerals, considerable data have been accumulated from investigation of pre-Cambrian diabases in Ontario. Since these rocks form well-defined geologic units and are in part genetically related to silver-cobalt deposits of world renown, we are presenting here the minor element determinations now in hand for these rocks. Discussion is limited to a statistical presentation of the data and a comparison of our abundance values with those of others on rocks of similar composition.

No special geologic study has been made of these diabases, as their general field relations are well known and we have adopted the current nomenclature. Neither has any special petrographic examination been made, beyond routine inspection of thin sections to determine 1) presence or absence of olivine, 2) granophyric texture, 3) the degree of alteration. Fig. 1 shows a key map of the general area.

Selection and Preparation of Material

No difficulty was encountered in finding suitable exposures of the various diabases, as road cuts and lake shores are almost everywhere available. Deep weathering is likewise not a problem in this recently glaciated terrane. Single hand specimens or aggregate samples weighing 2–3 pounds were collected. Reduction of the samples for spectrochemical work was carried out according to the procedure outlined below** No special precautions regarding contamination

* This investigation is part of a general program of geochemical research carried on in the Department of Geology, M.I.T., under contract with the Office of Naval Research, Washington, D.C.

** As sample preparation of this kind is an important feature of the investigation, we are including details as follows:

1. Break up the hand specimen into pieces small enough to feed into a laboratory-size jaw crusher. (Smaller specimens may be fragmented in a screw vise; larger ones may require a sledge hammer.)
2. Select one to two pounds of the freshest rock fragments for the jaw crusher. Save on fragment for a thin section.
3. Clean the jaw crusher. Run through it several rock fragments of the specimen to decontaminate

Fig. 1. Key map to general area.

of the material need to be taken during this initial processing since addition of traces of foreign elements would be below the detection limit relative to this size of sample. Screening, however, is avoided because of selective sizing shown by grains of contrasting shapes. Some dust is unavoidably lost from each sample but this is not believed to affect appreciably the analytical work.

---

it and discard these. Pass remaining fragments through the crusher at least three times, setting the jaws closer for each run ($\frac{1}{4}''$ down to $\frac{1}{8}''$).

4. Thoroughly mix crushed particles by rolling on a square piece of paper or rubberized cloth. Cone and quarter the sample; *i.e.*, spread it out over a circular area and quarter it with a knife or spatula. Select one quarter and store the remainder in a glass jar. Label with specimen number.

5. Separate coarse from fine fragments in the quarter which has been retained. Pulverize the coarse fragments either in a diamond percussion mortar or by passing them through steel rolls and combine with the fines. All equipment must be cleaned before using.

6. Cone and quarter again and repeat process of separating and pulverizing any remaining coarse particles until a sample of the desired size is obtained. This quantity will about half fill a 2 gm sample bottle.

7. Grind sample to fineness with a mechanical mortar and pestle. This operation usually requires about one-half hour. The mortar and pestle is first decontaminated by grinding a small quantity of the unknown; this is discarded.

8. Bottle and label the product in 7.

Analytical Procedure, Calibration and Precision

Spectrochemical procedures were used throughout, as outlined by Ahrens [1]; details of procedure will be published later. Synthetic standards were used for all determinations except for potassium, for which standard diabase W-1 (Fairbairn *et al.* [2]) and a single point working curve (Ahrens [3]) were employed. On the basis of chemical and flame photometer determinations by several analysts, the potassium content in W-1 averages at 0·69 %. Determinations based on the use of synthetic standards were calibrated with standard diabase W-1 so as to reduce possible systematic error as much as possible. Consider cobalt for example. The cobalt

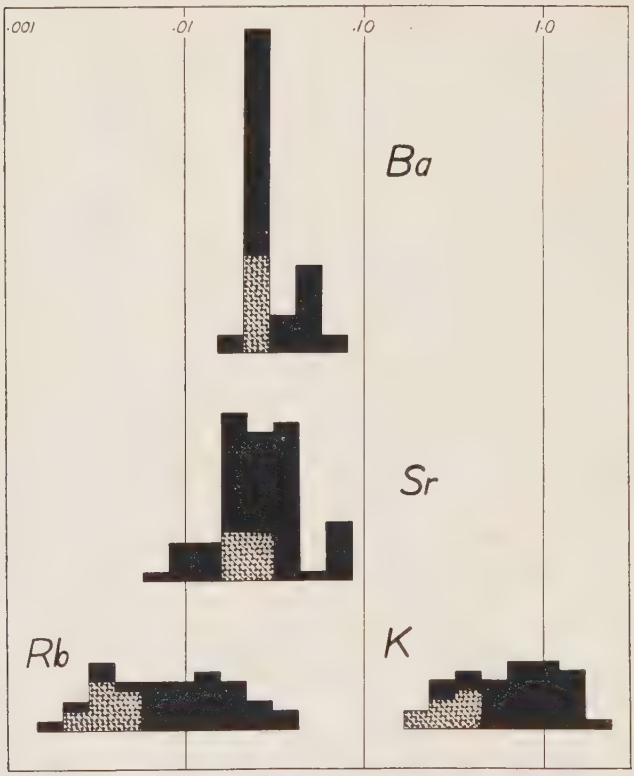

Fig. 2. Frequency distribution diagram for Ba, Sr, Rb and K.

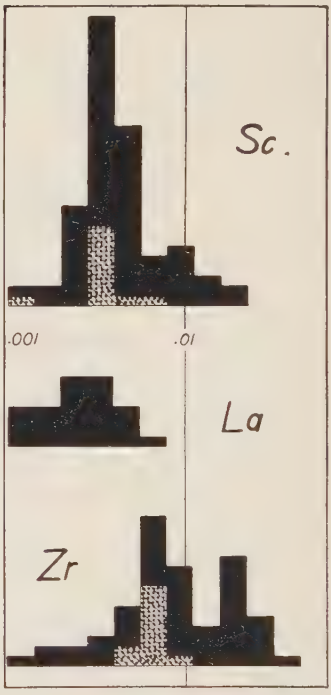

Fig. 3. Frequency distribution diagram for Sc, La and Zr.

content of diabase W-1 as obtained from a mean of three spectrochemical determinations (separate laboratories) and one chemical determination is 0·0033 %. The value obtained in the Cabot Spectrographic laboratory, M.I.T., is 0·003 %. The ratio 1·1 is used as a "correction" factor and all cobalt determinations are multiplied by this factor. Other constituents are treated in the same way. In order that such a "correction" factor is to be of any real significance, each constituent must be determined *precisely* in W-1 (mean of several determinations); otherwise the "correction" may merely indicate the random deviation of the particular determination and not a systematic error inherent in the method.

The reader may refer to Ahrens [1] for information on the precision of the spectrochemical determinations. In general, relative errors for all constituents fall within the range of 3–8 %.

Results of Analyses

Table 1 includes data for 16 elements in 59 diabase specimens. The specimens are classified as Nipissing (with or without granophyre), post-Nipissing (containing

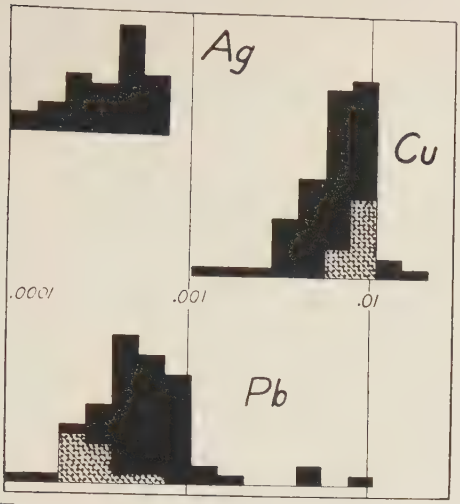

Fig. 4. Frequency distribution diagram for Ag, Cu and Pb.

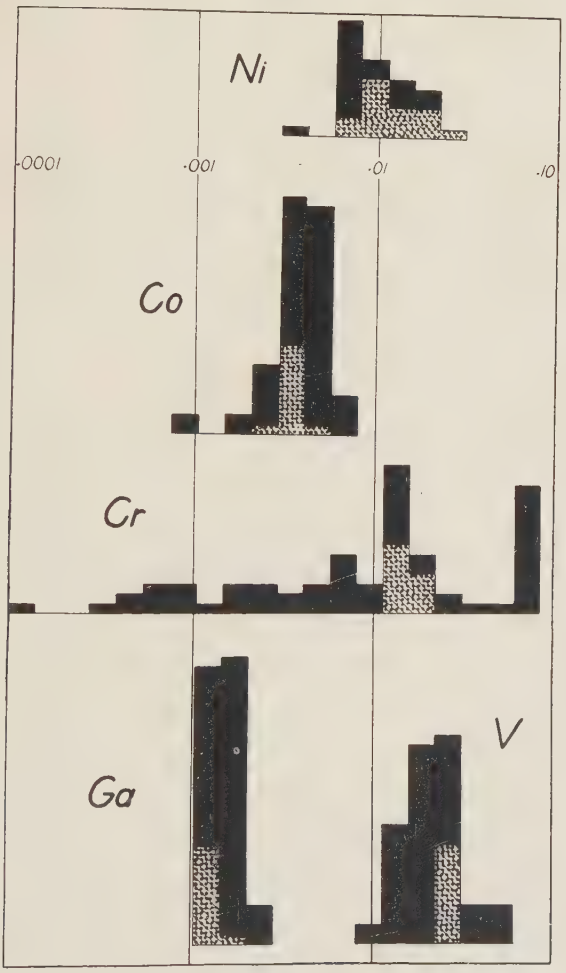

Fig. 5. Frequency distribution diagram for Ni, Co, Cr, Ga and V.

Table 1. % concentration of various

(A dash — indicates that concentration is below detection

Locality No.	*Type of diabase*	Ni	Co	Cr	V	Cu	Ag
1145	Nipissing		0·0044	~0·0005	>0·043	0·0028	—
1314	Nipissing granophyric		0·0035	0·0025	0·019	0·0090	—
1317	Nipissing	0·0065	0·0044	0·001	0·18	0·0071	~0·00009
1319	Nipissing granophyric		0·0038	~0·00077	0·023	0·0057	—
1320	Nipissing granophyric		0·0041	0·00067	~0·034	0·0099	—
1321	Nipissing granophyric		0·0010	0·00036	0·0039	0·0012	—
1326	Nipissing granophyric	0·0072	0·0050	0·0059	0·0026	0·0080	—
1328	Nipissing	0·0061	0·0042	0·0027	0·021	0·0097	—
1450a	Nipissing granophyric		0·0024	0·0037	0·020	0·0019	0·00038
1451a	Nipissing granophyric		0·0010	0·00073	0·030	0·0033	0·00047
1453	Nipissing altered	0·012	0·0022	0·077	0·021	0·0065	0·00017
1459	Nipissing altered	0·0074	0·0041	0·012	0·017	0·0052	0·00056
1470	Nipissing granophyric		0·0044	0·00092	~0·043	0·0084	0·00057
1475	Nipissing altered		0·0053	0·015	0·013	0·0062	0·00026
1483	Nipissing altered		0·0024	0·0019	0·019	0·0062	0·00067
1485	Nipissing altered	0·012	0·0023	>0·077	0·014	0·0067	0·00054
1489	Nipissing	0·018	0·0044	>0·077	0·015	0·0074	0·00049
1492	Nipissing altered	0·020	0·0052	>0·077	0·021	0·0081	0·00076
1493	Nipissing altered		0·0074	>0·077	0·016	0·0054	0·00063
1493a	Nipissing		0·0064	>0·077	0·016	0·0045	0·00045
1494	Nipissing olivine	0·0075	0·0049	0·0052	0·013	0·0041	0·00045
1496	Nipissing olivine	0·0073	0·0039	0·015	0·026	0·0044	0·00049
1497	Nipissing sheared		0·0060	>0·077	~0·043	0·0073	0·00029
1499	Nipissing granophyric		0·0032	0·023	~0·026	0·0074	0·00014
1501	Nipissing olivine	0·0079	0·0043	~0·0077	0·017	0·0052	0·0003
1509	Nipissing		0·0030	~0·077	0·020	0·0077	0·00069
1518	Nipissing	0·019	0·0047	~0·077	0·015	0·0058	0·00071
1521	Nipissing olivine		0·0067	~0·054	0·014	0·0055	0·00037
1527	Nipissing altered		0·0030	>0·077	0·019	0·0068	0·00016
1531	Nipissing granophyric		0·0046	0·0018	~0·043	0·0083	0·00047
1536	Nipissing granophyric		0·0034	0·021	0·023	0·0068	0·00019
1539	Nipissing granophyric		0·0022	0·0004	0·015	0·0035	0·00026
1542	Nipissing		0·0049	0·038	0·033	0·0073	0·00025
1147	Matachewan		0·0036	0·012	0·014	0·012	—
1318	Matachewan granophyric	0·0041	0·0033	0·0035	0·018	0·011	—
1322	Matachewan	0·012	0·0043	0·012	0·017	0·0089	—
1323	Matachewan		0·0037	0·016	0·017	0·011	—
1324	Matachewan		0·0038	0·0061	0·012	0·0033	—
1352	Matachewan		0·0038	0·0085	0·015	0·011	—
1550	Matachewan altered	0·0079	0·0016	0·013	~0·026	0·0096	0·00032
1146	Post-Nipissing (with olivine)		0·0054	0·017	0·015	0·0074	—
1148	Post-Nipissing (with olivine)		0·0030	0·002	0·018	0·0048	—
1316	Post-Nipissing (with olivine)		0·0047	0·0077	0·039	0·0032	—
1329	Post-Nipissing (with olivine)	0·0071	0·0043	0·0043	0·012	0·0041	—
1503	Post-Nipissing (with olivine)	0·0089	0·0058	0·023	0·024	0·0055	0·00058

minor elements in Ontario diabase

limit and a blank that no determination was made)

Pb	Sc	La	Zr	Ga	Ba	Sr	Rb	K	Li
0·0083	0·0052	~0·001	0·013	0·0018	0·025	0·025	0·010	0·63	
0·001	0·0044	~0·001	0·010	0·0013	0·015	0·013	0·013	0·84	
0·0024	0·0038	—	0·006	0·0015	0·025	0·025	0·018	1·34	
0·0043	0·0052	0·0025	0·014	0·0017	0·01	0·017			
0·001	0·0044	—	0·0069	0·0019	0·03	0·042	0·016	0·96	
0·0053	0·0027	0·0046	0·026	0·0017	0·03	0·017			
0·00068	0·0048	0·001	0·009	0·0014	0·025	0·042			
0·00054	0·0038	—	0·009	0·0018	0·02	0·034	0·013	0·60	
0·00049	0·0037	0·0019	0·010	0·0021	0·03	0·0086	0·013	1·01	
0·00036	0·0038	0·0036	0·017	0·0026	0·015	0·0059			
0·00032	0·0032	—	0·0035	0·0015	0·01	0·0085	0·007	0·46	
0·00019	0·0044	—	0·0054	0·0017	0·03	0·034			
0·0003	0·0043	0·0012	0·008	0·002	0·03	0·042	0·007	0·75	
0·00062	0·0037	0·0014	0·007	0·0017	0·049	0·042	0·018	1·17	
0·0013	0·0037	0·0022	0·016	0·0024	0·049	0·042			
0·00072	0·0044	—	0·0019	0·0017	0·025	0·021			
0·0004	0·0044	—	~0·0016	0·0015	0·0069	0·0085	0·002	0·25	
0·00052	0·0061	—	0·0013	0·0019	0·02	0·017			
0·00075	0·0039	~0·0017	0·009	0·0015	0·03	0·021	0·009	0·56	
0·00062	0·0037	~0·001	0·0061	0·0013	0·03	0·021			
0·00046	0·0023	0·0028	0·018	0·002	0·039	0·042			
0·00048	0·0027	0·0044	0·0023	0·0021	0·049	0·042			
0·00062	0·0039	0·0026	0·017	0·0017	0·03	0·042	0·015	0·66	
0·00092	0·0052	tr.	0·0055	0·0016	0·01	0·021			
0·00042	0·0023	0·0034	0·019	0·002	0·039	0·042	0·007	0·93	
0·00058	0·0040	—	0·0028	0·002	0·0069	0·013			
0·0015	0·0041	—	0·0026	0·0015	0·01	0·021	0·004	0·32	
0·00072	0·0038	—	~0·0019	0·0013	0·01	0·013			
0·00039	0·0044	—	0·0031	0·0017	0·0069	0·017	0·004	0·38	
0·00077	0·0048	~0·0021	0·008	0·0022	0·0069	0·017	0·015	0·95	
0·00032	0·0044	—	0·004	0·0015	0·03	0·025	0·023	1·34	
0·0014	0·0048	0·0015	0·01	0·0026	0·03	0·025	0·01	0·87	
0·00047	0·0052	—	0·0058	0·0018	0·01	0·017	0·018	1·23	
~0·00008	0·0033	—	0·008	0·0013	0·039	0·063	0·035	1·61	
0·0012	0·0036	0·0023	0·014	0·0021	0·03	0·042	0·018	0·97	
0·00042	0·0034	—	0·009	0·0015	0·025	0·025	0·011	0·50	
<0·00025	0·0037	~0·0011	0·010	0·0015	0·015	0·021	0·008	0·52	
0·0011	0·0028	0·0045	0·025	0·0016	0·049	0·042	0·032	2·30	
0·00052	0·0043	0·0020	0·016	0·0018	0·074	0·063	0·03	1·67	
0·00072	0·0034	—	0·0054	0·0015	0·03	0·025	0·029	1·66	
0·0005	0·0029	0·0045	0·022	0·0015	0·049	0·063			
0·00079	0·0033	0·0059	0·019	0·0015	0·049	0·042	0·012	1·33	
0·00071	0·0030	0·0056	0·022	0·0015	0·025	0·042			
0·00067	0·0021	0·003	0·021	0·0016	0·049	0·063			
0·00071	0·0026	~0·001	0·006	0·0021	0·049	0·085			

Table 1

Locality No.	*Type of diabase*	Ni	Co	Cr	V	Cu	Ag
1506	Post-Nipissing (with olivine)	0·0086	0·0061	0·012	0·018	0·0058	0·00026
1691	Nipigon (olivine)	0·015	0·0033	0·013	0·026	0·0086	—
1692	Nipigon (olivine)	0·012	0·0034	0·016	0·028	0·0093	—
1693	Nipigon	0·0011	0·0036	0·013	0·030	0·01	—
1694	Nipigon	0·012	0·0035	0·017	0·028	0·009	—
1695	Nipigon (olivine)	0·011	0·0034	0·014	0·026	0·0091	—
1696	Nipigon (olivine)	0·011	0·0030	0·016	0·021	0·0069	—
1697	Nipigon	0·0082	0·0028	0·015	0·028	0·0074	—
1698	Nipigon (olivine)	0·016	0·0041	0·015	0·023	0·007	—
1699	Nipigon (olivine)	0·011	0·0032	0·012	0·023	0·0082	—
1700	Nipigon (olivine)	0·009	0·0032	0·01	0·023	0·0102	—
1701	Nipigon (olivine)	0·008	0·0029	0·010	0·025	0·0095	—
1704	Nipigon	0·0078					
1705	Nipigon (olivine)	0·017					
1200	Duluth gabbro		0·0019	0·0011	0·010	0·0084	0·00043
1208	Duluth gabbro		0·0055	0·011	0·028	0·011	0·00054
1209	Duluth gabbro		0·0036	0·0057	0·017	0·016	0·00037

olivine), Matachewan (with or without granophyre facies), and Nipigon (almost all with olivine). In addition there are 3 specimens of Duluth gabbro.

Histograms have been drawn (Figs. 2 to 5) which bring out the important details of the table. The abscissa is a log scale, the ordinate linear; the class interval is based on an arbitrary power factor of 1·4, whereby each successive interval is 1·4 time greater (or smaller) than its immediate neighbour. This method of presentation is particularly suited to comparison of data having a large numerical range. The height of a column representing *one* analysis is shown (for example) at the left side of the nickel histogram.

The histograms are arranged as far as practicable so that elements having common characteristics are grouped together. Each is plotted so as to indicate the relative level of concentration (*e.g.* K, Ba; Cu, Ag). The relative dispersion of the analyses about a peak (usually central) is also evident (moderate dispersion about an ambiguous peak in rubidium; low dispersion in gallium).

The dotted areas in the histogram represent analyses of the Nipigon diabase only; the solid black include all other diabases. Preliminary examination of the data showed that the Nipigon type had lower dispersion than any of the other diabases and could be shown to advantage by a separate pattern in the histograms. Further contrasts are noted in Table 2.

The conspicuous features of the histograms and of Table 2 are:

1. The relatively restricted range shown by all elements in the Nipigon diabase, with the single exception of nickel.

2. Detectable silver ($>0{\cdot}0001\,\%$) is restricted to the Nipissing diabase.

3. The correlation between potassium and rubidium—both low in the Nipigon, both high in the Nipissing.

(Continued)

Pb	Sc	La	Zr	Ga	Ba	Sr	Rb	K	Li
0·00053	0·0026	0·0027	0·013	0·0021	0·049	0·063	0·005	0·65	
0·00030	0·0032	—	0·006	0·0012	0·027	0·023	0·0031	0·33	0·00075
0·00032	0·0037	—	0·0073	0·0012	0·025	0·021	0·00341	0·33	0·00059
0·00061	0·0036	—	0·010	0·0015	0·025	0·021	0·0042	0·46	0·00079
0·00023	0·0041	—	0·008	0·0012	0·025	0·021	0·0032	0·33	0·00056
0·00032	0·0037	—	0·0067	0·0012	0·025	0·021	0·0032	0·33	0·00062
0·00022	0·0033	—	0·0056	0·0014	0·025	0·019	0·0021	0·21	0·00045
0·00021	0·0011	—	0·0055	0·0014	0·03	0·025	0·00245	0·21	0·00056
0·00023	0·0057	—	0·0060	0·0015	0·03	0·025	0·0034	0·33	0·00064
0·00029	0·0032	—	0·0069	0·0016	0·03	0·025	0·0042	0·46	0·00074
0·00034	0·0032	—	0·0068	0·0014	0·03	0·025	0·0046		0·0011
0·00041	0·0032	—	0·0068	0·0013	0·03	0·025	0·0054		0·0012
0·0003	0·0015	0·0026	0·022	0·0023	0·03	0·025			
0·00045	0·0019	0·0033	0·021	0·002	0·03	0·034	0·01	0·79	
0·00074	0·0022	0·0036	0·033	0·02	0·03	0·025			

Table 2. Summary of data in Fig. 3–6 and Table 1

Element	*Nipissing and post-Nipissing*	*Matachewan*	*Nipigon*
Ba	Fairly low dispersion	Fairly low dispersion	Very low dispersion. Mean ~ mean of other diabases
Sr	Moderate dispersion	Moderate dispersion	Very low dispersion. Mean ~ mean of other diabases
Rb	High dispersion	Mean is higher than overall mean	Low dispersion. Mean is lower than overall mean
K	High dispersion	Mean is higher than overall mean	Low dispersion. Mean is lower than overall mean
Sc	High dispersion. Relatively high symmetry in histogram outline	No distinctive characteristic	Low dispersion (one analysis excepted). Mean ~ mean of other diabases
La	Moderate dispersion. No distinctive characteristic	Moderate dispersion. No other distinctive characteristic	Not analyzed
Zr	Post-Nipissing diabase mostly at high end of histogram	Mean is at high end of histogram	Low dispersion. Mean ~ mean of other diabases
Ag	Fairly low dispersion	Below 0·0001% (detection limit)	Below 0·0001% (detection limit)
Cu	Fairly high dispersion	Mean somewhat higher than for Nipissing diabases	Low dispersion. Mean somewhat higher than for other diabases
Pb	High dispersion definite mean	No distinctive characteristic	Relatively low dispersion. Mean lower than for other diabases

Table 2. (Continued)

Element	*Nipissing and post-Nipissing*	*Matachewan*	*Nipigon*
Ni	Mean not centrally placed	No distinctive characteristic	Dispersion not distinctive. Mean somewhat higher than overall mean
Co	Fairly low dispersion with strong central maximum	No distinctive characteristic	Relatively low dispersion. Mean somewhat lower than overall mean
Cr	Very high dispersion. Granophyric diabases on low end of histogram	Moderate dispersion only, with mean overall mean	Low dispersion, with mean somewhat higher than overall mean
V	Moderate dispersion. Symmetrical histogram	No distinctive characteristic	Very low dispersion. Mean somewhat higher than overall mean
Ga	Low dispersion	Same as Nipissing	Very low dispersion. Mean somewhat lower than overall mean

4. The wide range for chromium (high dispersion) compared with a much more restricted range for the sister-element vanadium.

5. The narrow range of values for gallium.

Comparison with other Diabases and Allied Rocks

Lithium

Because lithium determinations are confined to a limited number (11 specimens), it is not possible to obtain accurate information about its dispersion in diabase. In the Nipigon specimens, the lithium concentration ranges from 0·00045 to 0·0012% and averages at 0·0007%. Strock [4] gives an average of 0·001% for basalt and gabbro, and Wager and Mitchell [5] report a similar magnitude, though a little less (average ~0·0005%), in some specimens of basalt and dolerite from various localities; these authors report a lower magnitude from Skaergaard gabbro. Further support of a general magnitude of 0·0005 to 0·001% is given by lithium determinations (unpublished data) in a suite of 16 specimens of Columbia River basalt from near Portland, Oregon. The concentration range is from 0·0007 to 0·018% and the average is 0·0012% Li.

Table 3. Average abundance of several elements in Ontario diabase

Element	*Average** (%)	*No. of specimens analyzed*
Ni	0·011	32
Co	0·0039	57
Cr	0·022	57
V	0·022	57
Cu	0·0072	57
Pb	0·00087	57
Sc	0·0037	57
Zr	0·010	57
Ga	0·0017	57
Ba	0·028	57
Sr	0·03	57
Rb	0·011	40
K	0·8	38
Li	0·0007	11

* For mean values for Ag and La see text

Potassium and rubidium

Both elements show a moderate degree of scatter. Potassium averages at close to 1%, which is about what would be expected on the basis of previous compilations; for example, Daly [6]. Rubidium averages at 0·0012%. The association and abundance of these two elements in common igneous rocks and meteorites is discussed in some detail by Ahrens, Pinson and Kearns [7].

Strontium and barium

Strontium and barium show little scatter in this suite of specimens and average at 0·03% and 0·028% respectively. Table 4 compares the strontium value with others given in the literature.

Table 4. Average strontium values for gabbro and diabase

Description	% Sr	*Reference*
German gabbro	0·017	Noll [8]
Gabbro	0·014	Hevesy and Würstlin [9]
Gabbro and dolorite, from southern Lapland	0·008	Sahama [10]
Basic rocks, Roslagen, Sweden	0·015	Lundegårdh [11]
Dolerite and basalt, various	0·01	Wager and Mitchell [5]
Original Skaergaard magma	0·035	Wager and Mitchell [5]
Ontario diabases	0·03	This investigation

See also analyses by Nockolds and Mitchell [12].

Data on barium are much scantier and whereas there is general accordance in the various published strontium values, such is not the case for barium. Von Englehardt [13] gives an average of 0·006% in gabbro, basalt and anorthosite and Wager and Mitchell [5] give a magnitude of 0·002% for some specimens of basalt and dolerite and 0·004% for original Skaergaard magma. On the other hand, Tröger [14] gives an average of 0·025% which is about the same as that given in this paper. (The average barium value in standard diabase W-1, based on determinations by three spectrochemists and one chemist, is 0·03%.) It is not known to what extent the barium variations are real; the general impression is that analytical differences have played a considerable part.

Gallium

It has been known for some time that gallium is rather uniformly dispersed in igneous rocks. This is amply borne out quantitatively in Fig. 5 which shows gallium to be unique in this respect among the elements discussed here.

The average concentration of 0·0017% agrees closely with chemical determinations of Sandell [15] and also with magnitudes reported by Goldschmidt and Peters [16], Nockolds and Mitchell [12] and Wager and Mitchell [5], all of whom used spectrochemical methods.

Copper

Most copper determinations fall within the range of 0·005 to 0·01%. In their study on North American igneous rocks, Sandell and Goldich [17] have reported many copper determinations in diabase and equivalent compositional types. In general their results are somewhat higher than those given here and average at 0·015% (they range from ~0·002 to 0·03%) as compared with a mean of 0·009% found in this investigation. Sandell and Goldich may be consulted for references to several earlier publications on copper determinations in igneous rocks.

Lead

The mean lead content is 0·0009%. Occasional specimens show a considerable enrichment to as much as 0·005 to 0·01%; if these are omitted, the average is reduced to ~0·0006%. These magnitudes agree closely with those of Sandell and

Goldich [17] for similar compositional types. Specimens from Nipigon are characteristically low and average at ~0·0003%. At these low concentrations which verge on the detection limit concentration of the method used here, the accuracy of the determinations is much lower than, say, above 0·001%.

Scandium

Scandium shows a moderate scatter and averages at 0·0037%. This does not accord with the value of 0·00065% given by Goldschmidt and Peters [18] and is closer to, but considerably higher than an average of 0·002% given by Sahama [10] for dolerite and gabbro from southern Lapland. It should be recalled that all these specimens have been calibrated with standard diabase W-1 and that the average scandium content of this specimen based on the determinations of four spectrochemists is 0·0045%. Although scandium is not easily accepted by olivine (Wager and Mitchell [5]) there is no detectable lowering of scandium in olivine diabase. Such rocks are, of course, not real olivine rocks and determinations by Pinson [19] show clearly that the scandium concentration is low in dunite and serpentine and averages at 0·0009%, compared with 4 times this amount in diabase and basalt.

Zirconium

Zirconium shows a considerable scatter. Its concentration ranges from 0·001 to 0·06% and averages at 0·01%. This average is similar in magnitude, though lower than that of 0·014% given by Hevesy and Würstlin [20] for gabbro. Wager and Mitchell's [5] values for Skaergaard gabbro average at 0·003%; in the original magma the concentration of zirconium is given as 0·005%.

Cobalt

Cobalt has a small dispersion. Such behaviour might be anticipated because of the close association of cobalt and magnesium in silicate rocks (Sandell and Goldich [17]). The magnesium concentration does not vary greatly in diabase, but some scatter in the cobalt concentration could be caused by the presence of significant quantities of sulphide minerals. The average cobalt abundance in these specimens is 0·004%. This is similar to the value of 0·005% for North American diabase and basalt, reported by Sandell and Goldich [17]; their value is based on chemical determinations and on the well developed geochemical coherence of cobalt and magnesium in silicates. Wager and Mitchell [5] and Nockolds and Mitchell [12] report similar cobalt concentrations in rocks of like chemical composition.

Nickel

Nickel shows a moderately uniform dispersion not much unlike that of cobalt. Because of the considerable variety of diabase specimens which are represented, this is a little surprising because nickel is very sensitive to fractionation and a greater scatter might have been anticipated. Thus, Wager and Mitchell [5] report 0·017% nickel in marginal gabbro from Skaergaard; earliest olivine gabbro shows as much as 0·1% and this drops to 0·004% in so-called middle gabbro and below 0·0002% in the next member (hortonolite ferrogabbro) of the Skaergaard layered series.

Table 5 compares the average nickel content for diabase reported here (0·011%) with values given elsewhere in the literature for allied rock types. Agreement is

moderately good, which again is surprising because of the behaviour of nickel referred to above. An earlier publication by Vogt [22] gives the somewhat higher magnitude of 0·03% Ni as the average for diabase, basalt and compositional equivalent.

Table 5. Nickel in basic rocks

Description	% Ni	*Source*
Average gabbro	0·016	Goldschmidt [21]
Keweenawan flow, rocks from Michigan, and Minnesota diabase	0·018	Sandell and Goldich [17]
Gabbro and diabase from southern Lapland	0·0045	Sahama [10]
Basic rocks, Roslagen, Sweden	0·0065	Lundegårdh [11]
Marginal Skaergaard	0·017	Wager and Mitchell [5]
Ontario diabase	0·011	This investigation

Vanadium

Dispersion is moderately small for all specimens and vanadium averages at 0·022%. This is higher than the average of 0·0056% given by Sahama [10] for gabbro and dolerite from southern Lapland and is similar to averages of 0·032% for mafic rocks from Roslagen, Sweden (Lundegårdh [11]) and like magnitudes for Skaergaard gabbro reported by Wager and Mitchell [5].

Chromium

Chromium shows by far the greatest scatter and is unique in this respect; surprisingly enough the chromium concentration in Nipigon diabase appears to remain virtually constant. Because of the extremely large scatter, the average value of 0·022% is of less significance than other values. This magnitude is similar to a value of 0·034% reported by Goldschmidt [21] for average gabbro, and a value 0·041% for gabbro and dolerite from southern Lapland (Sahama [10]) Wager and Mitchell [5] report several similar magnitudes in Skaergaard gabbro as well as various other concentrations. Their publication clearly shows the extremely sensitive behaviour of chromium during differentiation, and thereby illustrates the fact that average values for chromium in diabase, basalt and gabbro do not have the same significance as averages for other constituents.

Silver

There is a scarcity of reliable information on the abundance of silver in igneous rocks. Although several silver determinations have given in this paper, it is doubtful, however, whether the position is much improved for diabase because the values are generally less reliable than those of the other constituents given here. This is mainly due to the extremely low concentration of silver in most specimens and also to the fact that detectable concentrations of silver are sometimes observed in high-grade electrodes. However, it is quite probable that magnitudes are usually moderately reliable in most specimens. Silver could be determined in 32 specimens and in these it averages at 0·0004%. If we assume that the concentration in the other specimens is small by comparison, the average silver value for diabase, and presumably basalt and gabbro, is reduced to about 0·0002%. It is of interest that detectable concentrations are confined to the Nipissing diabase, which in the Cobalt district is associated with high-grade silver-bearing veins.

Lanthanum

Lanthanum could be determined in 26 specimens, for which its average is 0·003%. If we assume, as in the example of silver, that the lanthanum concentration in the other specimens is considerably smaller by comparison, the average for all specimens is reduced to ~0·0015%. This is somewhat greater than an average of 0·0009% given by Goldschmidt [22] for average gabbro.

Acknowledgments—In addition to the overall sponsorship of this work by the Office of Naval Research (see page 34), we wish to acknowledge special assistance in collection of material, preparation of samples, and draughting of illustrations by W. G. Johnston and F. B. Whiting. We wish also to express appreciation to Dr. W. L. C. Greer of the Ontario Department of Mines for assistance in obtaining material from Lake Nipigon.

References

[1] Ahrens, L. H.; Quantitative spectrochemical analysis of silicate rocks, silicate minerals and allied materials. Spectrochim. Acta 1951 **4** 302. [2] Fairbairn, H. W., Schlecht, W. G., Stevens, R. E., Dennen, W. H., Ahrens, L. H. and Chayes, F.; A co-operative investigation of precision and accuracy in chemical, spectrochemical and modal analysis of silicate rocks. U.S. Geological Survey Bulletin, 1951 (No. 980). [3] Ahrens, L. H.; Spectrochemical analysis. Addison-Wesley, Cambridge, Mass. 1950. [4] Strock, L.: Zur Geochemie des Lithiums. Nachr. Ges. Wiss. Göttingen, Mat.-phys. Kl. 1936 **4** (No. 15) 171. [5] Wager, L. R. and Mitchell, R. L.; The distribution of trace elements during strong fractionation of basic magma—a further study of the Skaergaard intrusion, East Greenland. Geochim. et Cosmochim. Acta 1951 **1** 129. [6] Daly, R. A.; Igneous rocks and the depth of the earth. McGraw Hill, New York 1933. [7] Ahrens, L. H., Pinson, W. H. and Kearns, M. M.; Association of rubidium and potassium and their abundance in common igneous rocks and meteorites. Geochim. et Cosmochim. Acta 1952 **2** 229. [8] Noll, W.; Geochemie des Strontiums. Chem. Erde 1934 **8** 507. [9] Hevesy, G. v. and Würstlin, K.; Über die Häufigkeit des Strontiums. Z. anorg. allgem. Chem. 1934 **216** 312. [10] Sahama, Th. G.; Spurenelemente der Gesteine im südlichen Finnisch-Lappland. Bull. Comm. géol. Finlande, 1945, No. 135. [11] Lundegårdh, Per. H.; Rock composition and development in Central Roslagen, Sweden, Arkiv. Kemi, Mineral. Geol. 1946 **23**A (No. 9). [12] Nockolds, S. R. and Mitchell, R. L.; The geochemistry of some Caledonian plutonic rocks: a study in the relationship between major and trace elements of igneous rocks and their minerals. Trans. Roy. Soc. Edinburgh 1948 **56** 533. [13] Engelhardt, W. von; Die Geochemie des Barium. Chem. Erde 1936 **10** 187. [14] Tröger, E.; Der Gehalt an selteneren Elementen bei Eruptivgesteinen. Chem. Erde 1935 **11** 286. [15] Sandell, E. B.; The gallium content of igneous rocks. Amer. J. Sci. 1949 **247** 40. [16] Goldschmidt, V. M. and Peters, Cl; Zur Geochemie des Galliums. Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl. 1931 **1** 165. [17] Sandell, E. B. and Goldich, S. S.; The rarer metallic constituents of some American igneous rocks. I. Jour. Geol. 1943 **51** 99; II. *Ibid.* 167. [18] Goldschmidt, V. M. and Peters, Cl; Zur Geochemie des Scandiums. Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl. 1931 **1** 257. [19] Pinson, W. H.; Trace element studies in meteorites and rocks and the origin of meteorites. Ph.D. Thesis, 1951, Dept. of Geology, M.I.T. [20] Hevesy, G. v.. and Würstlin, K.; Die Häufigkeit des Zirkoniums. Z. anorg. allgem. Chem. 1934 **216** 305. [21] Goldschmidt, V. M.; Geochemische Verteilungsgesetze der Elemente. IX. Die Mengenverhältnisse der Elemente und der Atom-Arten. Skrift. Norske Vid. Akad. Oslo, Mat.-nat. Kl. 1937 (No. 4). [22] Vogt, J. H. L.; Nickel in igneous rocks. Econ. Geol. 1923 **18** 307.

Geochimica et Cosmochimica Acta, 1953, Vol. 3, pp. 47 to 52. Pergamon Press Ltd., London

Was ist Laterit?

P. Schaufelberger

(Received 17 September 1951)

ABSTRACT

According to Meigen and Lang, laterite is formed in the absence of humus; it is a rock. In the presence of humus, the hydrargillite changes into kaolinite, which is found in all tropical soils. Since laterite is an intermediary product of weathering, its appearance and composition are constantly undergoing change. To place the emphasis on the process, the red soils of the tropics are formed by laterisation, which is followed, however, by kaolinisation. Several products are formed: laterite and various soils.

Nach der bodenkundlichen Literatur soll der Laterit ein typischer tropischer Boden sein, nach den Geologen ist er ein Verwitterungsprodukt dieses Klimas. Wer hat nun recht? Da er nun sehr selten ist, wurde er oft mit roten Unterböden verwechselt, die sich in allen Klimaten bilden, und es ist leicht in der Literatur eine Beschreibung zu finden, die auf einen solchen Unterboden zutrifft. Nach den Untersuchungen von Warth und Meigen geht hervor, daß der Laterit aus den Hydroxyden von Aluminium und Eisen bestehen soll und das Aluminiumhydroxyd als Hydrargillit auftritt. Was ist nun typisch für den Laterit? P. Ehrenberg äußert sich darüber folgendermaßen: „Man kann entweder eine Eigenschaft des zumeist als Laterit bezeichneten Erdbodens als wichtigstes Kennzeichen herausgreifen: etwa die rote Farbe der Verwitterungsmasse, die man in Deutschland nach dem Vorgange von G. C. du Bois neuerdings vielfach als maßgebend anzusehen scheint, und die auch J. Walther, dessen Ausführungen mir sonst von besonderer Wichtigkeit zu sein scheinen, ebenfalls in den Vordergrund stellen will. Man kann den Gehalt an Eisenkonkretionen als entscheidend hervorheben, wie dies zuerst F. Wohltmann, dann nach ihm z. B. P. Vageler tat, oder wie P. Gürich und ihm folgend jetzt J. Walther, das Hauptgewicht auf den Vorgang der Lateritbildung selbst legen."

Ist nun der Laterit ein Boden oder ein Gestein? Als basenarme rote Böden kämen folgende in Frage:

Urwaldboden Nr. 1081

Ort: Cali-Dagua; Meereshöhe 1970 m.
Klima: Temperatur ca. 19° C; Regenmenge ca. 3500 mm; Regenfaktor ca. 190.
Vegetation: Wald.
Topographie: 20° Neigung.
Muttergestein: Diabas.

Profilbeschreibung

	Boden	*Unterboden*
Mächtigkeit (cm)	20	80
p_H	3·05	4·50
Humus (%)	17·02	3·14
Farbe	braun	erst gelb, dann rot

Chemische Zusammensetzung

	Boden %	*Unterboden* %	*Diabas* %
SiO_2	37·19	37·18	49·13
Al_2O_3	12·16	22·08	16·67
Fe_2O_3	9·33	23·66	12·69
MgO	0·75	0·77	4·48
CaO	1·15	0·97	9·22
Na_2O	1·22	1·03	6·36
K_2O	0·03	0·08	0·68

Analytiker: A. Uribe

Kaktusboden Nr. 1267

Ort: La Unión (Valle de Cauca); Meereshöhe 1140 m.
Klima: Temperatur ca. 24° C; Regenmenge ca. 900 mm; Regenfaktor unter 40.
Vegetation: Ackerland und Weide.
Topographie: 30° Neigung.
Muttergestein: Diabas.

Profilbeschreibung

	Boden	*Unterboden*
Mächtigkeit (cm) . . .	30	70 + *x*
p_H	7·6	8·5
Humus (%)	1·18	0·58
Farbe	braun	rot

Chemische Zusammensetzung

	Boden %	*Diabas* %
SiO_2	48·30	53·24
Al_2O_3	15·42	14·71
Fe_2O_3	10·74	14·53
MgO	3·01	6·69
CaO	3·72	10·08
Na_2O	1·48	3·62
K_2O	0·29	1·04

Analytiker: J. Parra, A. Alarcón

Diesen kolumbianischen roten Böden sei das Profil eines afrikanischen Lateritbodens von H. Jacques-Félix und R. Bétrémieux beigegeben.

Lateritboden von Akonolinga

2–25 cm: Braunschwärzlicher Horizont, reich an Feinwurzeln, gröbere Bestandteile aus Quarz und sehr harten Konkretionen sind nicht häufig. Die Grenze zum unteren Horizont ist scharf.

25–65 cm: Heller, gelbrötlicher Auswaschungshorizont, poröse, sehr zerreibliche Aggregate; an gröberen, analogen Bestandteilen ist er etwas reichlicher als der Boden.

65–115 cm: Sehr reich an Lateritknollen (75%), identisch, aber größer als in den oberen Horizonten. Die obere Grenze ist scharf und parallel der Oberfläche. Dieser Horizont ist heller als der vorige.

115–*x* cm: Unter 115 cm liegt der kompakte Lateritpanzer, ungefähr in 1 m Mächtigkeit aufgeschlossen. Dieser Panzer ist nicht kontinuierlich und gelegentlich zeigen sich senkrechte Verwerfungen, deren Spalten mit Material der oberen Horizonte gefüllt sind und in sie treiben die Bäume auch ihre Wurzeln. Der Panzer kann auch fehlen, dann liegen die Lateritknollen des oberen Horizontes direkt auf dem Muttergestein, einem typischen Gneis.

Der Urwaldboden zeigt, wie der Podsol der gemäßigten Zone, ein starkes Auswaschen der Basen, eine Anreicherung der Kieselsäure im Boden und der Sesquioxyde im Unterboden. Vergleichen wir den Unterboden mit dem Muttergestein, so stellen wir eine Abwanderung der Basen und der Kieselsäure fest, ähnlich wie beim Laterit. Aber wie schon H. Stremme gezeigt hat, erfolgt die Zufuhr der Sesquioxyde vom Boden zum Unterboden, sie ersetzen nicht nur die abgewanderten Basen, sondern reichern sich absolut an und daher ist die unbewegliche Kieselsäure relativ in geringerer Menge vorhanden. Die röntgenologische Untersuchung der Tone dieses Bodens ergab die Anwesenheit von schwachen Hydrargillit- und starken Kaolinitlinien. Da nach M. Bauer und C. W. Correns der Feldspat immer erst in Hydrargillit zerfällt, dieser also erst später in einen Ton übergeht, so überrascht seine Anwesenheit nicht.

Die Kaktusböden des ariden Klimas zeigen nicht immer eine basische Reaktion. Wie schon H. Jenny gezeigt hat, reagieren sie auch sauer, bis p_H 4·8. Sie sind humusarm und die Sesquioxyde werden wenig oder nicht verlagert, sonst aber

gleichen sie in ihrem chemischen Verhalten den Urwaldböden. Beide Böden unterscheiden sich chemisch von den Lateriten dadurch, daß Kieselsäure angereichert wird. Andere kolumbianische Böden des ariden Klimas zeigen ebenfalls schwache Hydrargillit- und starke Kaolinitlinien.

In den übrigen Klimaten Kolumbiens gibt es ebenfalls rote Unterböden; die ebenfalls Kaolinit enthalten, aber weniger basenarm sind, ja sogar basenreich. Was nun die Bodenbildung im wechselfeuchten Klima anbetrifft, so finden wir einmal endoperkolative Böden, zu denen auch der Kaktusboden gehört, und im ariden und semiariden, also bei Regenfaktoren unter 60, auch Alkaliböden, zu denen Grundwasser kapillar in der Trockenzeit aufsteigt. Dies ist aber, in Übereinstimmung mit Mohr, nur möglich, wenn der Grundwasserspiegel nicht tiefer als 2 bis $2^1/_2$ m liegt. Diese sehr fruchtbaren Böden zeigen in Kolumbien eine Bodenreaktion zwischen p_H 7–8·7. Da bei ihnen die Comberreaktion versagt, so besteht keine Gefahr, daß die üppige Vegetation durch Lateritpanzer verdrängt werde.

Nach Richthofen (H. Stremme) soll sich der Laterit unter Wald bilden. Diesem Laterit könnten folgende Profile entsprechen.

Lateritprofil von Manizales

Meereshöhe: 2100 m.
Klima: Temperatur 17·5° C; Regenmenge 2140 mm; Regenfaktor = 122.
Profilbeschreibung:

a) Vulkanische Asche
   6. Waldboden ($p_H = 5$) . . . . . 40 cm
   5. Vulkanische Asche, leicht gelblich . . . . . 450 cm
   4. Weißer, zerreiblicher (Hydrargillit) . . . . . 20 cm

b) Vulkanische Tuffe
   3. Blutrote Eisenkonkretion. . . . . 5 cm
   2. Übergangszone, rot bis rosa . . . . . 15 cm
   1. Graue Tuffe. Von der Übergangszone dringen 20 bis 60 cm lange, stalaktitähnliche Eisenkonkretionen senkrecht in die Tiefe und bilden die Fleckzone . . . . . $200 + x$ cm

Lateritprofil von Pereira

Ort: Cestilal-Bach; Meereshöhe 1480 m.
Klima: Temperatur ca. 20° C; Regenmenge ca. 2200 mm; Regenfaktor ca. 110.
Profilbeschreibung:

a) Vulkanische Asche
   7. Waldboden (p_H unter 5·5) . . . . . 40 cm
   6. Vulkanische Aschen . . . . . 350 cm
   5. Weißer Ton . . . . . 40 cm

b) Oberer vulkanischer Tuff
   4. Roter vulkanischer Tuff, an einer Stelle an der Base gebleicht (0–40 cm) . 300 cm

c) Unterer vulkanischer Tuff
   3. Limonitkruste. . . . . 2 cm
   2. Fleckzone. Direkt unter dem Limonit bis 5 cm gebleicht, dann tiefrot mit gelben Flecken, unten gelb mit roten Flecken . . . . . 80 cm
   1. Weißer Ton . . . . . $10 + x$ cm

Strasse

NB. Nach mündlicher Mitteilung, die ich Herrn J. Velásquez verdanke, der die Gegend bodenkundlich kartierte, findet man in der untersten Bleichschicht (1) in 50 cm Tiefe Grundwasser.

Beide Profile liegen unter Waldböden (p_H 4·5 bis 5·5), was auch mit den Regenfaktoren übereinstimmt. Der weiße Ton von Manizales ist in heißer Salzsäure schwer löslich, und die Lösung gab mit Ammoniak einen weißen Niederschlag. In heißer Schwefelsäure ist er unlöslich; es handelt sich also um Hydrargillit.

Entsprechen nun diese beiden Profile wirklichen Lateriten? Bei Manizales liegt die Bleichzone über dem Eisenpanzer und der Fleckzone, also in anderer Anordnung als bei den Profilen von Walther und Lacroix (P. Ehrenberg), beim Profil von Pereira fehlt der Eisenpanzer unter der obersten Bleichschicht, aber im roten Tuff finden wir wenigstens an einer Stelle die untere Bleichzone, aber die Fleckschicht fehlt, aber als solche dürfte der Horizont 2, unter dem Limonitpanzer in Frage kommen. Die vulkanischen Tuffe unter den Aschen sind immer rot, meist fehlt in Kolumbien, wie in Costa Rica, der oberste Bleichhorizont; die Ausbildung dieses Horizontes, sowie des Eisenpanzers hängt offenbar von der Durchlässigkeit der Tuffe ab, d. h. ob sie Grundwasser ansammelt oder nicht. In solchen Fällen ist man leicht geneigt, die Tuffe für rote fossile Böden zu halten. Eine Bodenbildung in den Tuffen vor Ablagerung der Asche ist sehr wahrscheinlich, aber da, wo sie nicht mit Asche bedeckt sind oder waren, sind sie erst gelblich verwittert.

R. Lang schildert die indischen Laterite folgendermaßen: „Beim Betrachten der in Indien immer wieder auftretenden Profile: oben Braunerde, unterhalb Laterit, kann man auf den Gedanken kommen, daß etwa das Wasser zunächst der Erdoberfläche überall da, wo Pflanzenreste in größerer Menge als humusbildende Bestandteile im und am Boden liegen, Braunerde erzeugt, und allmählich in eine Zone durchsickert, in der es, von der Mitwirkung von Humussubstanzen befreit, Lateritbildung verursacht.“ Da Lang den Laterit für fossil hält, sucht er zu beweisen, daß Braunerde und Laterit sich nicht gleichzeitig bilden könne.

Da sich in den Tropen viele braune Böden bilden, so kann es sich auch um Böden trockenerer Klimate handeln. Beim Kaktusboden werden die Basen gelöst und bei Anwesenheit von Alkalien- oder Kalziumionen ist Eisen nicht beweglich. Bei den Bambusböden werden die Alkalien, beim Caliboden das Kalzium abtransportiert, sie entsprechen braunen und kastanienbraunen Steppenböden. Im semihumiden Klima liegt die Bodenreaktion zwischen 5·5–6·5, so daß das Eisen nicht oder nur sehr wenig beweglich ist, so daß dann das Muttergestein der indischen Braunerde jünger wäre als der Laterit.

In Kolumbien handelt es sich um Waldboden, der sauer reagiert, daß Eisen im Boden und Muttergestein löslich ist; es bildet in ihm möglicherweise die Bleichzone. In der feldspatführenden unteren Schicht wird das Eisen ausgefällt durch die Alkalien dieser Mineralien. Dadurch wird die Lösung alkalisch und die Kieselsäure wird entfernt, es bilden sich Limonit und wohl Goethit und Hydrargillit. Diese erste Etappe dauert so lange, bis die Alkalien verbraucht sind. In der zweiten Etappe werden bei saurer Lösung die Erdalkalien angegriffen. In der dritten Etappe sinkt die Bodenreaktion unter p_H 5·5, so wird das Eisen gelöst, es bildet sich der untere Bleichhorizont und später die Fleckzone; der Laterit wird zum Bauxit. Der Laterit ist ein Zwischenprodukt und ändert Aussehen und chemische Zusammensetzung, so daß es leicht verständlich ist, wenn Chemiker und Mineraloge zu verschiedenen Schlüssen kommen. Es kann ganz gut die Bleichzone und der Eisenpanzer fehlen.

Aus diesen Tatsachen geht deutlich hervor, daß beim Laterit, wie es Ehrenberg annimmt, das Hauptgewicht auf den Vorgang zu legen ist. Es muß aber zwischen

zwei Vorgängen unterschieden werden: Entfernung durch Hydrolyse der Kieselsäure, der Alkalien und Erdalkalien; an der Oberfläche wird aber der Laterit bald in irgendeinen Boden übergehen, deswegen ist jener so selten, oder Lösung des Eisens in der Oberschicht, was eine saure Reaktion verlangt, und Ausfällen dieses Metalls in der unteren und Beginn der Laterisation. In beiden Fällen ist eine Vorbedingung notwendig, die vor 40 Jahren MEIGEN erkannt hat, die *Abwesenheit von Humus*. Ist Humus anwesend, dann geht der Hydrargillit in Kaolinit über. Ist die Ansicht MEIGENs richtig, dann muß die reine Gesteinsverwitterung der Lateritbildung entsprechen. Glücklicherweise gibt es einige Analysen von Verwitterungsprodukten und ihrer Muttergesteine.

Verwitterung in der Wüste

	Sandstein I		*Sandstein II*		*Grauwacke*		*Granit*		*Gneis*		*Pegmatit*	
	Zersatz	*frisch*	*Zersatz*	*frisch*	*Zersatz*	*frisch*	*Zersatz*	*frisch*	*Zersatz*	*frisch*	*Zersatz*	*frisch*
si .	399	2230	178	748	259	403	274	295	151	336	222	474
al .	28	3	30·5	21	48·5	14·5	38	36·5	31	45	33	49
fm .	29	56	20·5	30	45·5	72·5	27	24	35	19	28·5	10
c . .	27	14	32	28·5	3·5	8	13	13	24	9·5	24·5	6
alk .	16	27	17	20·5	2·5	5	22	26·5	10	26·5	14	35

Literatur: BLANCK und PASSARGE

Gesteinsverwitterung

	Java I		*Java II*		*Georgia I*		*Distr. of Columbia*		*Georgia II*	
	Zersatz	*Andesit*	*Zersatz*	*Andesit*	*Zersatz*	*Granit*	*Zersatz*	*Granit*	*Zersatz*	*Gabbro*
si . . .	170	270	41	142	210	323	293	303	61	94
al . . .	56	29	61	30	71	44·5	40	37	50	21·5
fm . .	43	35	36	33·5	20	10	33	29	45	32·5
c . . .	0	24	0·5	24·5	0·5	9	12·5	15	2	39
alk . .	1	11	2·5	12	8·5	36·5	14·5	19	3	7
Literatur:	BLANCK und OLDERSHAUSEN		MOHR		NIGGLI		NIGGLI		NIGGLI	

In der Wüste beobachten wir die erste Etappe der Lateritbildung: Die Alkalien und die Kieselsäure werden entfernt, bei alkalienreichen Gesteinen (Gneis und Pegmatit) auch Aluminium, das nach MOHR bei einem p_H über 7·5 oder unter p_H 4·5 beweglich ist. Bei der alkaliarmen Grauwacke hat auch die Lösung des Kalziums begonnen.

In den feuchteren Klimaten finden wir die zweite Etappe, es sind neben Kieselsäure und Alkalien auch die Erdalkalien stark ausgewaschen worden. M. BAUER hat den Hydrargillit ebenfalls in der Verwitterungskruste gefunden. Die Lateritbildung ist reine Gesteinsverwitterung und geht jeder Bodenbildung voraus.

Legt man nach dem Vorschlag von P. GÜRICH, P. EHRENBERG das Hauptgewicht auf den Vorgang: Hydrolyse oder Eisenausfällung + Hydrolyse, dann erklären diese Vorgänge, warum die Unterböden sich rot verfärben; entweder durch Hydrolyse wie beim Kaktusboden oder Eisenausfällung im Urwaldboden und Podsol.

In den extremen Klimaten (Kaktus- und Urwaldboden) ist die Lateritbildung stärker betont als die Bodenbildung. Aber bei diesen Vorgängen bilden sich zwei verschiedene Produkte: Hydrargillit bei Abwesenheit von Humus; dieses Verwitterungsprodukt ist der Laterit oder ein Gestein; bei Anwesenheit von Humus bildet sich Kaolinit oder irgendein Boden. Der Laterit kann sich dann auch als Oberflächen- oder Tiefenlaterit bilden. In allen diesen Theorien steckt ein Körnchen Wahrheit.

Zusammenfassung

Nach Meigen und Lang bildet sich Laterit bei Abwesenheit von Humus, er ist ein Gestein; bei Anwesenheit von Humus geht der Hydrargillit in Kaolinit über, den wir in allen tropischen Böden finden. Da der Laterit ein Zwischenprodukt der Verwitterung ist, ändert er ständig sein Aussehen und seine Zusammensetzung. Legt man das Hauptgewicht auf den Vorgang, dann bilden sich die roten Böden der Tropen durch Laterisation, der aber eine Kaolinisation folgt. Es bilden sich verschiedene Produkte: Laterit und verschiedene Böden.

Benützte Literatur

Bauer, Max; Beiträge zur Geologie der Seyschellen, insbesondere zur Kenntnis des Laterites. N. Jahrb. f. Min. etc. 1898. Blanck, E. und Oldershausen, E.; Über die Verwitterung von Andesit auf Java. Chemie der Erde, 1932 **7**. Planck, E. und Passarge, S.; Die chemische Verwitterung in der ägyptischen Wüste. Hamburg 1925. Correns, C. W.; Die Tone. G. Rundschau 1938. Ehrenberg, P.; Die Bodenkolloide. Dresden und Leipzig 1922. Jacques-Félix, H. und Bétrémieux, R.; Etude de quelques sols tropicaux. Bull. Agr. du Congo Belge 1949 **40** No. 1. Jenny, H.; Greath soil groups in the equatorial regions of Colombia S.A. Soil Science 1948 **66**. Meigen, W.; Laterit. G. Rundschau 1911. Mohr, E. C. J.; Der Boden der Tropen im allgemeinen und von Niederländisch-Indien insbesondere. Ref. D. Ern. d. Pfl. 1948 **30**. Schaufelberger, P.; Wie verläuft die Gesteinsverwitterung und Bodenbildung in den Tropen, insbesondere in Kolumbien. Schw. Min. u. Petr. Mitt. 1950 **30** No. 2. Schaufelberger, P.; La Laterita y los suelos rojos y amarillos. An. d. Edafología etc. Madrid 1951 **10** No. 2. Stremme, H.; Laterit und Terra rossa als illuviale Horizonte humoser Waldböden. G. Rundschau 1914. Lang, R.; Besteht die Möglichkeit gleichzeitiger lateritischer und nicht lateritischer Verwitterung in den Tropen ? Centralbl. f. Min. etc. 1915 (No. 5) 148–160. Niggli, P.; Petrographische Provinzen der Schweiz. Vierteljahresschrift der Naturforschenden Gesellschaft in Zürich. 1919 **74** (No. 1/2) 179–212.

Editor's Note

A recent paper by Silverman * gives a value of 140° C as the temperature of formation of some Brazilian quartz. The authors, however, neglected to add a pressure correction of 63° C. The determined temperature of formation, therefore, should be 203° C and the temperature coefficient for $SiO_3 - H_2O$ (liq.) should be $-0{,}085$ instead of $-0{,}128$.

Earl Ingerson

* Silverman, Sol R.: The Isotope Geology of Oxygen, Geochim. et Cosmochim. Acta, 1951 **2** 26–42.

Now available

INTERNATIONAL TABLES FOR X-RAY CRYSTALLOGRAPHY

Vol. I. SYMMETRY GROUPS

Demy quarto, bound in cloth, xii + 558 pages, 237 figures
(in English)

Editors:

N. F. M. HENRY and K. LONSDALE

Published for the

INTERNATIONAL UNION OF CRYSTALLOGRAPHY

by The Kynoch Press, Birmingham 6, England

CONTENTS

1. Historical Introduction, by M. von Laue
2. Crystal Lattices
3. Point-group (Crystal-class) Symmetry
4. Space-group Symmetry
5. Notes on Special Topics
6. Index of Symbols of Space Groups
7. Dictionary of Terms in English, French, German, Russian and Spanish

Price £ 5·5 s inclusive of postage and packing from The Kynoch Press (cheques should be made payable to Imperial Chemical Industries Ltd., Metals Division) or from any bookseller

Lange, Maxwell & Springer Ltd.

SCIENTIFIC, MEDICAL AND TECHNICAL BOOKSELLERS

take this opportunity to announce that they have established a special division within their organisation to handle exclusively the supply of Scientific, Technical and Medical literature to Industrial and Educational Research Organisations and Libraries

This division offers the following services:

- **Regular News Service** regarding newly published books and journals in all languages on Scientific, Technical and Medical subjects, contained in the LANGE, MAXWELL & SPRINGER BOOK NEWS sent free of charge on request
- **Supply of books and periodicals** on Subscription, published anywhere and in any language. Prices charged are at the official rate of exchange
- **Supply of Rare and Out-of-Print Books, Sets and Runs of Periodicals**
- **Translations of Foreign language Articles** undertaken
- **Hand-binding in our own bindery:** Speedy service at competitive prices
- **Books sent on approval if required**
- **Purchase or exchange** of surplus books and journals

We shall be pleased to arrange for our Representative to call in order to discuss with you any problems you may have with regard to the supply of Scientific, Technical and Medical literature

LANGE, MAXWELL & SPRINGER LTD.

41–45 NEAL STREET, LONDON, W.C.2

Telephone: Temple Bar 1124

Printed by Universitätsdruckerei H. Stürtz AG., Würzburg